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Establishment of Design Criteria for Optimum Burners for Application to Heavy Fuel Fired Package Boilers Volume 1. Laboratory Scale Tests

Energy and Environmental Research Corp.
Irvine, CA

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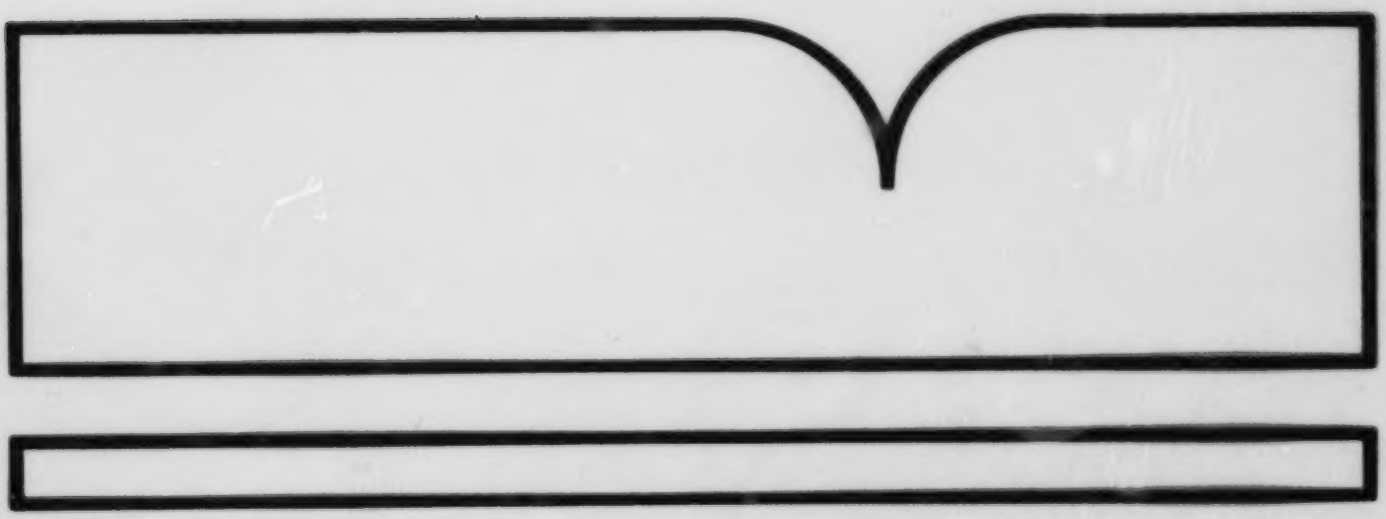

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THE ESTABLISHMENT OF DESIGN CRITERIA FOR OPTIMUM BURNERS FOR APPLICATION TO HEAVY FUEL FIRED PACKAGE BOILERS

Volume I. Laboratory Scale Tests

by:

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16. ABSTRACT The report gives results of a research program to develop low-NOx heavy oil burners for application to industrial package boilers. Volume I documents Phase 1 of the program, bench scale studies which defined optimum conditions for two-stage combustion. This information led to a conceptual two-stage low-NOx burner design. Volume II gives results of pilot scale experiments conducted in two test facilities with nominal capacities of 0.9 and 2.9 MWt, including tests of commercial burners for both firetube and watertube boilers. A wide range of petroleum-, coal-, and shale-derived fuels were investigated. Tests were also conducted with prototype advanced low-NOx burners which demonstrated that NOx emissions below 100 ppm (corrected to 0% O2) could be achieved almost independently of the bound nitrogen content in the fuel. The conceptual design was successfully scaled from 21 kWt to 0.9 MWt to 2.9 MWt with similar NOx emissions performance.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution Combustion	Pollution Control	13B 21B
Burners	Stationary Sources	13A
Design	Burner Design	14G
Boilers	Package Boilers	
Nitrogen Oxides	Staged Combustion	07B
Heavy Oils		11G

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PREFACE TO VOLUME I

This final report is the first of two volumes describing the work carried out under EPA Contract 68-02-3125. Volume I includes bench-scale experimental results and a review of commercial package boiler/burner designs. Volume II includes pilot-scale experimental results and conclusions with respect to optimum low-NO_x burner designs. Volume II also contains a comprehensive summary of the results and conclusions presented in both volumes.

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1.0 INTRODUCTION

This report describes the results of a research program to develop criteria for the design of low NO_x heavy oil burners for package industrial boilers. Package boilers are a subset of a class of equipment normally described as industrial boilers which include a wide range of design types and fuel capability. Industrial boilers are normally considered to be those boilers with a design firing rate between 10×10^6 and 500×10^6 Btu/hr. Those referred to as packaged are boilers designed and constructed as a self-contained unit, thus allowing them to be easily shipped and installed. They are available in firing capacities up to 350×10^6 Btu/hr input. Industrial boilers with firing capacities greater than this are normally shop-engineered and field erected.

In a 1978 environmental assessment study of stationary source NO_x control technologies by Waterland, et al., NO_x emissions from oil-fired package boilers accounted for 6.4 percent of total annual NO_x emissions in the United States. Although the increased utilization of coal provides a partial solution to the United States energy crisis, the realities of retrofit capability and process limitations necessitate that in the future many industrial users will continue to burn liquid fuels. Refinery operations will probably be geared to the production of premium fuels for transportation and industry and therefore industrial users will be required to burn heavy petroleum, coal, and shale-derived residual fuels. Since these liquid fuels have relatively high nitrogen contents and low hydrogen-to-carbon ratios, their use could cause adverse environmental impact due to the emission of combustion-generated pollutants unless appropriate control techniques are applied. The two pollutants of primary concern are nitrogen oxides (NO_x) and fine particulate matter. Because of this shift towards heavy high-nitrogen fuels, it appears likely that NO_x emissions from oil-fired package boilers will continue to be a significant and increasing fraction of the total NO_x emissions inventory.

1.1 Background

Nitrogen oxides emissions from stationary combustors can be reduced by combustion modification techniques which involve staging the heat-release process. However, the application of these techniques to residual fuel/oil-fired combustors has been only partly successful, because of a trade-off in pollutant emissions. The decrease in NO_x emissions is quite often accompanied by an increase in particulate emissions. The optimization of combustion modification techniques to control NO_x emissions from liquid fuel-fired combustors has also proved difficult because of the limited knowledge of the controlling phenomena.

The conversion of the nitrogen contained in liquid fuels can contribute significantly to the total nitrogen oxide (NO_x) emissions when such fuels are burned in stationary combustors. The amount of fuel NO (NO produced from fuel nitrogen) increases with increasing fuel nitrogen content. The other contribution to NO_x emissions, thermal NO (produced from molecular nitrogen) is dependent primarily on temperature and is relatively insensitive to fuel properties. Thus as fuel nitrogen content increases fuel NO constitutes an increased fraction of the total emissions. The formation of thermal NO is strongly dependent upon temperature, therefore combustion firing density and heat extraction influence the amount of thermal NO produced. Fuel NO formation is most strongly affected by fuel/air mixing conditions and is dependent upon burner design. Two factors are likely to increase the fuel nitrogen content of liquid fuels available for industrial use:

- reduced availability of high grade fuels and the need to burn heavy petroleum products;

- coal and shale-derived alternative fuels contain more nitrogen than the petroleum fuels they are supposed to replace.

Consequently it is advantageous to provide a technology which will allow high nitrogen fuels to be used without undue environmental impact.

There have been many studies concerned with the mechanism of fuel nitrogen oxidation which have resulted in the following simplified explanation. Initially the nitrogen in the fuel is released during thermal decomposition. The nitrogen-containing hydrocarbons are pyrolized and the primary nitrogen compound is probably HCN. The fate of this HCN is then almost totally determined by the local reactant stoichiometry:

- Fuel Lean. When oxygen is present the formation of NO is favored. For homogeneous premixed conditions, greater than 75 percent of fuel nitrogen could be converted to NO. The heterogeneous nature of liquid fuel combustion usually limits conversion to less than 50 percent (unless the fuel nitrogen content is low) and this is dependent upon atomizer and air delivery system design.

- Fuel Rich. In the absence of oxygen, N_2 is favored. Under fuel-rich conditions, nitrogen exists in the gas phase mainly as NO, NH_3 or HCN and the partition is dependent upon stoichiometry and temperature.

For typical fuels and combustion conditions, equilibrium XN concentrations (the sum of NO, HCN and NH_3 concentrations) are less than 10 ppm for mixtures containing between 60 and 70 percent of the theoretical air requirements. Thus if a combustor could be operated to achieve these near-equilibrium XN levels, fuel nitrogen conversion would be minimized.

Staged combustion is the modification of the combustion process to minimize fuel NO formation and, provided interstage heat removal occurs, thermal NO formation is also restricted. A staged combustion system is one in which the fuel is mixed with less than the total amount of air for complete combustion. Thus, in the first stage fuel nitrogen conversion to N_2 is maximized before the reactants become oxygen rich. This process can be achieved through burner design, which reduces the rate of fuel air mixing giving a fuel-rich zone internal to the flame, or by physically dividing the total air stream thus giving a well-defined fuel-rich zone. Under practical

conditions the limit of NO_x control for liquid fuels by staged combustion has normally been set by smoke emissions.

1.2 pose and Scope

The work which was conducted under this program was an extension of previous research and development carried out under EPA Contract 68-02-2624, which examined the effects of fuel properties and atomization parameters on the formation and control of NO_x in liquid fuel flames at both bench and pilot scale. That program sought to relate chemical and physical fuel properties to NO_x formation in liquid spray flames, and to investigate the interaction between liquid sprays and air flow patterns for conditions typical of package boilers under both staged and unstaged conditions.

The objective at the outset of this program was to extend the studies conducted under Contract 68-02-2624 to:

- document conceptual designs for low emission liquid fuel burners suitable for firetube and watertube package boilers;
- determine the optimum time/temperature/stoichiometry history during staged liquid fuel combustion in order to minimize NO_x and particulate emissions in advanced low emission burners and combustors;
- develop optimum atomizers for advanced low NO_x combustors;
- extend the prior fuel effects study to include a wide range of synthetic liquid fuels.

1.3 Approach

The overall technical approach for these studies was experimental, utilizing existing test facilities. A series of bench-scale experiments were conducted in a 21 kW (70,000 Btu/hr) downfired tunnel furnace to study

mechanisms of NO_x formation and control under normal and staged combustion. Both conventional and synthetic liquid fuels were injected into the furnace using an air-assist atomizer. The refractory-lined and insulated furnace was designed to allow controlled variation of mean stoichiometry and residence time through the use of injection ports at several axial locations. The heat extraction profile along the length of the furnace could also be varied by inserting water-cooled coils in these same ports. The furnace was capable of using artificial combustion "air" (e.g., mixtures of argon, oxygen, carbon dioxide, or other gases) which was used to (1) isolate fuel NO_x by replacing molecular nitrogen with argon/carbon monoxide, or (2) vary temperature by oxygen enrichment. Thus, the three main combustion variables of interest in staged combustion--temperature, time, and stoichiometry--could be controlled and varied independently in the bench-scale furnace. Analyses were conducted of the exhaust gas for major species and in-flame samples for both major species and minor nitrogeneous species.

Flames more typical of practical combustion systems were studied in two separate pilot-scale experiments. A 1 MW (3×10^6 Btu/hr) combustor which simulates the furnace of a Scotch marine firetube boiler was used to evaluate both commercial and experimental burners with a wide range of conventional and synthetic fuels. These studies were directed toward establishing the degree of NO_x control achievable through modification of conventional equipment and toward scaling of advanced concepts developed at bench scale. Both exhaust and in-flame gas samples were analyzed.

The second pilot-scale system was a 3 MW (10×10^6 Btu/hr) furnace which simulates the furnace environment of watertube boiler equipment. Combustion trials were conducted on a commercial watertube burner and two developmental low NO_x burners. The objectives of these experiments were similar to those of the firetube boiler studies. The advanced low NO_x burner concept was also investigated in this furnace, thus the development of accurate design and scaling criteria based on a fundamental understanding of the controlling mechanisms was possible.

Several fuels in addition to those already studied and characterized under Contract 68-02-2624 were included in the test program, bringing the total range of fuels to fourteen residual petroleum oils, three distillate petroleum oils, five shale-derived oils, and four coal-derived oils. Most of the fuels were analyzed for

- ultimate chemical composition;
- physical properties;
- distillation characteristics;
- nitrogen volatility;
- trace metals.

1.4 Report Organization

This report contains all experimental results achieved under Contract 68-02-3125. The report is divided into two volumes. This volume contains an overall description of the program background, objectives and organization; a review of commercial boiler/burner equipment (Section 2); a summary of the fuels considered in this program (Section 3.2); and results of the bench-scale studies (Section 3). Volume II discusses the results of the pilot-scale studies conducted at 1.0 and 3.0 MW scale and summarizes design criteria for advanced optimum low NO_x oil burners. Volume II also includes a comprehensive summary of both volumes.

2.0 REVIEW OF COMMERCIAL PRACTICE

One of the major program goals was to provide design concepts which would be compatible with existing package boiler equipment. Since it is unlikely that the major design features of industrial boilers is likely to change significantly over the next 30 years, a review of commercial firetube and watertube boiler/burner equipment was concluded. This information is gathered primarily from available literature, equipment manufacturers, and information gathered under EPA Contract 68-02-1500. This section of the report summarizes the design features of boiler/burner equipment, and reviews techniques for controlling NO_x emissions from industrial boilers.

2.1 Package Boiler Designs

Package boilers are a subset of a class of equipment normally described as industrial boilers which include a wide range of design types and fuel capability. Industrial boilers are normally considered to be those boilers with a design firing rate between 10×10^6 and 500×10^6 Btu/hr. In the upper end of the size range they are virtually indistinguishable from utility boilers. At the opposite end of the size range their characteristics are the same as commercial boilers. The subset referred to as packaged are boilers which are designed and constructed as an integral self-contained unit, thus allowing them to be easily shipped and installed. They are available in firing capacities up to 350×10^6 Btu/hr input. Industrial boilers with firing capacities greater than this are normally shop-engineered and field erected.

There are three major types of industrial boilers: watertube, firetube, and cast iron. Essentially all industrial boilers larger than approximately 50×10^6 Btu/hr heat input are watertube boilers. Firetube boilers generally have capacities in the range of 1×10^6 to 25×10^6 Btu/hr and cast iron boilers are even smaller, typically less than 10×10^6 Btu/hr capacity.

In a firetube boiler heat is released within a large cylindrical tube or a rectangular box submerged in water which is to be heated. If the chamber

is cylindrical it can be either horizontal, vertical or inclined. After passing through the combustion chamber further heat is extracted from the combustion products as they flow through bundles of firetubes placed in the water/steam mix. Firetube boilers have a relatively large water storage capacity for their design load, allowing them to effectively dampen fluctuations in the product steam characteristics over a very wide range of operating loads.

Most of the firetube boilers currently installed have internal furnaces; that is, the combustion chamber is enclosed in the boiler shell. In an external furnace arrangement, the boiler shell and combustion chamber are separate. Internal furnaces are preferred because of better water circulation and easier ash removal.

The principle applications of firetube boilers are steam producing for industrial processes and heating requirements for relatively large buildings. Boilers used for space heating application tend to be of lower capacity, producing hot water at 30 psig or 15 psig steam. Process steam generation applications may require steam pressure to be as high as 350 psig.

There are four major design categories of firetube boilers, and these are:

- Horizontal Return Tubular (HRT);
- Scotch Marine (Scotch);
- Firebox;
- Vertical.

In an HRT boiler, the firetubes are horizontal to the ground, the fuel firing mechanism is at one end, and the products of combustion make two, three, or four passes through the water medium. The furnace is set on rollers or suspended on hangers to allow for expansion and contraction. The boiler is encased with brick and is slightly sloped from front to rear. These boilers are well-suited for industrial use because they are compact and automatic and the initial cost is low.

In a two-pass HRT boiler, a refractory furnace is at the bottom corner of the unit. The products of combustion flow over a refractory bridge wall to the other end of the boiler. As the flue gas passes under the boiler, it heats the outer shell of the water basin. At the other end of the unit, the flue gases enter the firetubes. As the gases flow through the tubes, additional heat is transferred to the water producing steam or hot water. The gases are then exhausted through the stack.

In a four-pass boiler, the furnace is also at the end of the unit. The first pass goes through the furnace tube, which is an extension of the combustion chamber. The flue gases then pass beneath the furnace tube and then make two passes above the furnace tube. A forced-draft fan must be used to operate a four-pass HRT boiler.

HRT boilers are manufactured in various sizes ranging from approximately 0.5 to 20 x 10^6 Btu/hr heat input, with pressures of 15 to 250 psig. The smaller sizes are two-pass units and the larger sizes are four-pass units. HRT boilers offer longer boiler life, lower maintenance requirements, and higher firing rates than most firetube boilers. Water circulation through these units is poor, however, and thus the overall efficiency is only about 70 percent. These units were formerly the most popular type of firetube boiler; however, at present this design accounts for less than 10 percent of all commercial boilers.

A Scotch marine (Scotch) boiler comes in two-, three-, or four-pass units, consisting of a water-cooled furnace and well-cooled firetubes. A two-pass Scotch marine boiler and the furnace are contained in the same shell. The fuels are burned in the lower half of the unit. The products of combustion (flue gases) first flow through the furnace tube, heating the bottom of the water basin, then pass through the firetubes, heating the water in the top of the basin. The heat transfer from the gases in these tubes is enhanced by maintaining high velocities achieved by steadily decreasing the diameter or number of the tubes on each pass. Turbulators are also used to maintain high convective transfer rates. Baffles placed in the water circulation passages maintain relatively low bulk temperatures for the water

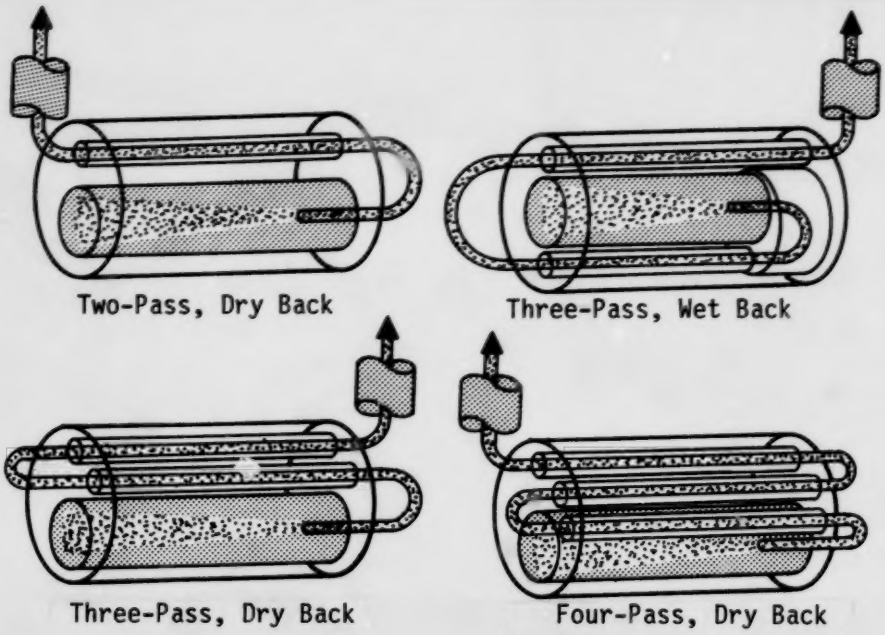
near the wall. Scotch firetube boilers were developed from the Scotch marine design over 30 years ago, and are currently the most popular type of firetube boiler. They are available in capacities up to 25,000 lbm steam/hr and the number of installed boilers is steadily increasing. A typical Scotch firetube boiler is shown in Figure 2-1. The major advantages of this design are its high operating pressure (normally 350 psig, but 600 psig is available in some instances) and the compact nature of the boiler.

Firebox boilers have a separate refractory-lined firing chamber essentially separate from the boiler drum. In some firebox units, the boiler drum is mounted directly over the firebox while in others the drum is horizontally adjacent to the firing chamber. Except for the floor, the furnace section is water jacketed and it is essential that the flame be shaped to closely match the geometry of the combustion chamber for optimum performance. The major advantages of this design type are its relatively high thermal efficiency and minimal space requirements. Firebox boilers are limited in firing capacity to 20,000 lbm steam/hr. Most firebox boilers are either the short type which have two internal tube passes, or the compact type which have three internal passes.

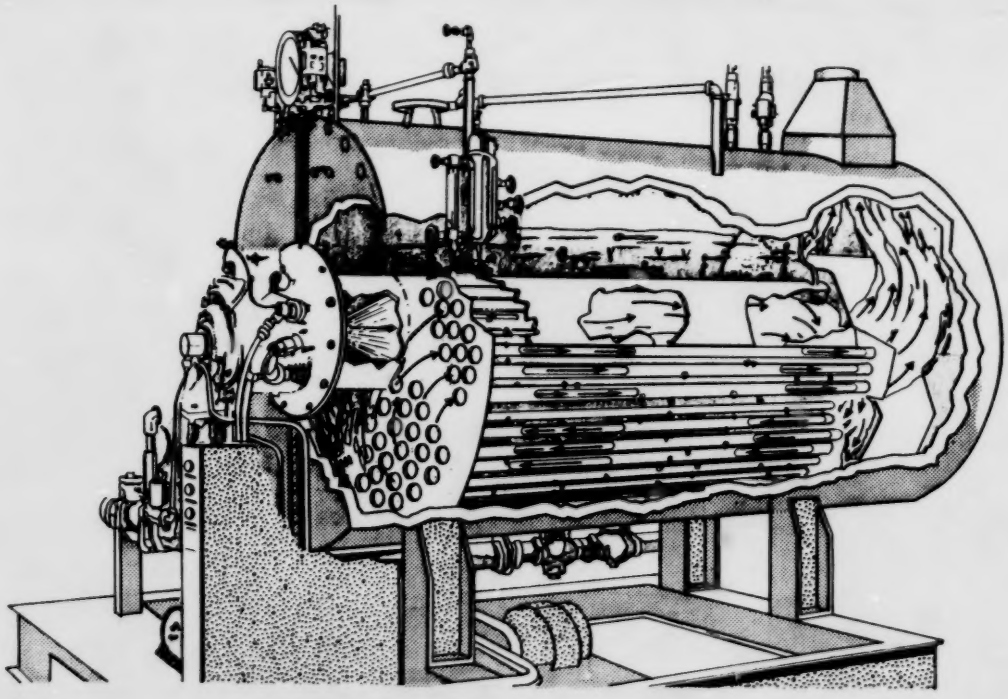
Vertical boilers are used for power boiler applications or as commercial hot water or steam boilers, and are normally single-pass units. The maximum capacity of these units is 3,500 lbm steam/hr and they have a maximum delivery pressure of 150 psig. The disadvantage of this design is the slow start-up procedure often necessary to prevent the steam-cooled upper tube end from overheating.

Firetube boilers normally operate with an excess air level of between 5 and 40 percent (depending upon turndown). The combustion chamber diameter varies from one to two feet, and the length-to-diameter ratio varies from six-to-one to ten-to-one. These boilers commonly operate on a high/low fire modulation with a forced draft system.

Firetube boilers generally have small compact firing chambers with a single burner. The firing intensity is generally much higher than for larger



a) Basic Gas-Flow Patterns in Scotch Boilers



(b) Dry-Back, Three-Pass, Gas-Fired Unit

Figure 2-1. Packaged Scotch boilers [2.1].

watertube boilers. However, the combustion chamber heat loss can vary widely from very low for refractory lined fireboxes to very high for long tubular firing chambers. The manufacturers of firetube boilers in the United States are listed in Table 2-1.

Watertube boilers can be either totally manufactured and shipped to the site (package boilers) or field erected. Boilers less than about 100 x 10^6 Btu/hr capacity are usually package boilers while units larger than about 250 x 10^6 Btu/hr capacity are always field erected.

One of the factors limiting the size of firetube boilers is the weight of water they contain. This problem is avoided in watertube boilers since water flows through the tubes, thus reducing its total volume. In a watertube boiler the hot combustion gases resulting from the combustion of fuel are in contact with the outside of the heat transfer tubes while the boiler water and steam pass through the tubes. The furnace walls are constructed of many small tubes either connected to form a membrane wall or independent tubes inside a refractory shell. The many individual tubes are interconnected with headers, steam drums or other equipment. The watertube construction allows very large furnaces to be constructed while maintaining small tube sizes. This minimizes the amount of steel required to contain the pressure and the total volume of water and steam in the boiler. This results in rapid heat transfer, good response to load changes and high overall boiler efficiency.

The type of construction utilized in watertube boilers is more able to withstand high steam pressures. This package boiler design is normally favored over firetube boilers for pressures in excess of 150 psig. All watertube boilers manufactured today are of the bent tube type. Straight watertube boilers have been superseded by bent watertube boilers in the intermediate size or by firetube boilers in the smaller size, although their design could be of importance from retrofit aspects because many are still in service. Bent tube boilers are classified by the number of drums, headers, and tube configuration. The watertubes form the combustion chamber walls, and are an integral part of the boiler. They are connected radially to the

TABLE 2-1. FIRETUBE BOILER MANUFACTURERS

The Bigelow Company New Haven, Connecticut	Kewanee Boiler Corporation Kewanee, Illinois
Boiler Engineering & Supply Company Phoenixville, Pennsylvania	James Leffel & Company Springfield, Ohio
Burnham Corporation Irvington, New York	North American Manufacturing Company Cleveland, Ohio
Cleaver-Brooks Division Milwaukee, Wisconsin	Orr & Sembower Middletown, Pennsylvania
Dunham-Bush Harrisonburg, Virginia	Oswego Package Boiler Company, Inc. Oswego, New York
Eclipse Lookout Company Chattanooga, Tennessee	Preferred Utilities Manufacturing Corp. Danbury, Connecticut
Hodge Boiler Works East Boxton, Massachusetts	Ray Burner Company San Francisco, California
Industrial Boiler Company Thomasville, Georgia	Superior Boiler Works, Inc. Hutchinson, Kansas
Industrial Combustion, Inc. Milwaukee, Wisconsin	Superior Combustion Industries, Inc. New York, New York
S. T. Johnson Company Oakland, California	Trane Company Burlington, Iowa
Johnston Boilers, Inc. Ferrysburg, Michigan	York-Shipley, Inc. York, Pennsylvania

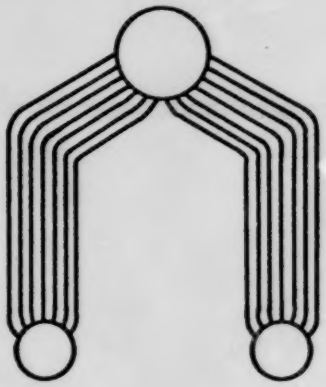
steam drum. The drum and headers are arranged in three general configurations (Figure 2-2). Forecasts indicate that by 1996 over 90 percent of all watertubes sold for oil or gas firing with a capacity up to 250 x 10^6 Btu/hr will be packaged units.

There is a wide range of industrial watertube boiler designs. Each manufacturer has built up empirical guidelines for specific applications based on years of experience. The primary variables affecting combustion are as follows:

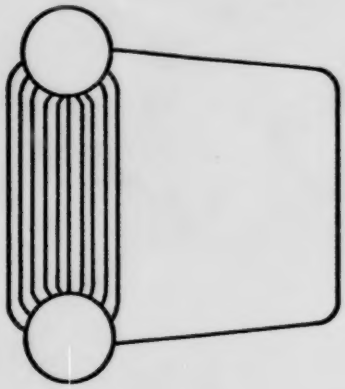
- Number of burners;
- Burner spacing;
- Configuration (single wall fired, opposed fired, tangential, etc.);
- Air heater discharge temperature;
- Furnace heat liberation rate or combustion intensity;
- Furnace heat absorption (related to heat liberation per cooled surface area);
- Firing depth.

The companies currently manufacturing watertube boilers in the United States are listed in Table 2-2. The four largest manufacturers are Babcock and Wilcox, Combustion Engineering, Foster Wheeler and Riley Stoker. Most watertube boiler manufacturers supply burners of their own design. However, there are a number of companies which supply burners for retrofit or for special customer requests. Table 2-3 lists current manufacturers of gas and oil burners in the United States.

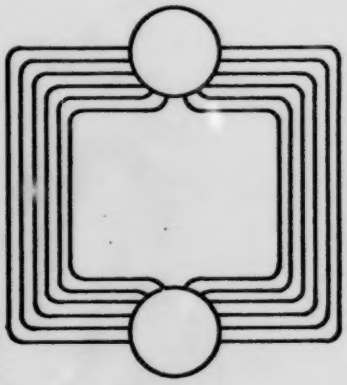
The general design features of watertube and firetube boilers can be compared in Figure 2-3. From a combustion viewpoint the major difference between the two boiler designs is the shape of the combustion chamber, which will accommodate different flame shapes. Thus, a long narrow flame is preferred for a firetube boiler, whereas a compact near-field dominated flame is normally employed in watertube boilers.



A-type has two small lower drums or headers. Upper drum is larger to permit separation of water and steam. Most steam production occurs in center furnace-wall tubes entering drum.



D-type allows much flexibility. Here the more active steaming risers enter drum near water line. Burners may be located in end walls or between tubes in buckle of the D, right angles to drum.



O-type is also a compact steamer. Transportation limits height of furnace, so, for equal capacity, longer boiler is often required. Floors of D and O types are generally tile-covered.

Figure 2-2. Drum and header configuration for bent tube packaged watertube boiler.

TABLE 2-2. WATERTUBE BOILER MANUFACTURERS

Ajax Boiler and Heater Company Gardena, California	Lasker Boiler & Engineering Corp. Chicago, Illinois
The Babcock & Wilcox Company Barberton, Ohio	Malsbary Manufacturing Company Oakland, California
The Bigelow Company New Haven, Connecticut	Nebraska Boiler Company, Inc. Lincoln, Nebraska
Boiler Engineering & Supply Company Phoenixville, Pennsylvania	Parker, Sid E., Boiler Mfg. Company Los Angeles, California
Bryan Steam Boiler Company Peru, Indiana	Riley Stoker Corporation Worcester, Massachusetts
Clayton Manufacturing Company El Monte, California	Superior Combustion Industries, Inc. New York, New York
Cleaver-Brooks Division Milwaukee, Wisconsin	Trane Company Burlington, Iowa
Combustion Engineering, Inc. Windsor, Connecticut	Vapor Corporation Chicago, Illinois
Foster Wheeler Corporation Livingston, New Jersey	Va-Power Besler Emeryville, California
International Boiler Works Company East Stroudsburg, Pennsylvania	Henry Vogt Machine Company Louisville, Kentucky
E. Keeler Company Williamsport, Pennsylvania	Zurn Industries Erie, Pennsylvania

TABLE 2-3. GAS AND OIL BURNER MANUFACTURERS

American Gas Furnace Company
Elizabeth, New Jersey

Babcock and Wilcox, Inc.
Barbertown, Ohio

Century Engineering Corporation
Cedar Rapids, Iowa

Clever Brooks Company
Milwaukee, Wisconsin

Combustion Engineering Corporation
Windsor, Connecticut

Coppus Engineering Corporation
Worcester, Massachusetts

Fredrick Cowan and Company, Inc.
Plainview, New York

Eclipse Fuel Engineering Company
Rockford, Illinois

Green Colonial Inc.
Des Moines, Iowa

E. Keeler Company
Williamsport, Pennsylvania

Lammert Industries, Inc.
Addison, Illinois

Maxon Premix Burner Company, Inc.
Muncie, Indiana

National Airoil Burner Company
Philadelphia, Pennsylvania

North American Manufacturing Co.
Cleveland, Ohio

Peabody Engineering Corporation
New York, New York

Ray Oil Burner Company
San Francisco, California

Riley Stoker Corporation
Worcester, Massachusetts

Selas Corporation of America
Dresher, Pennsylvania

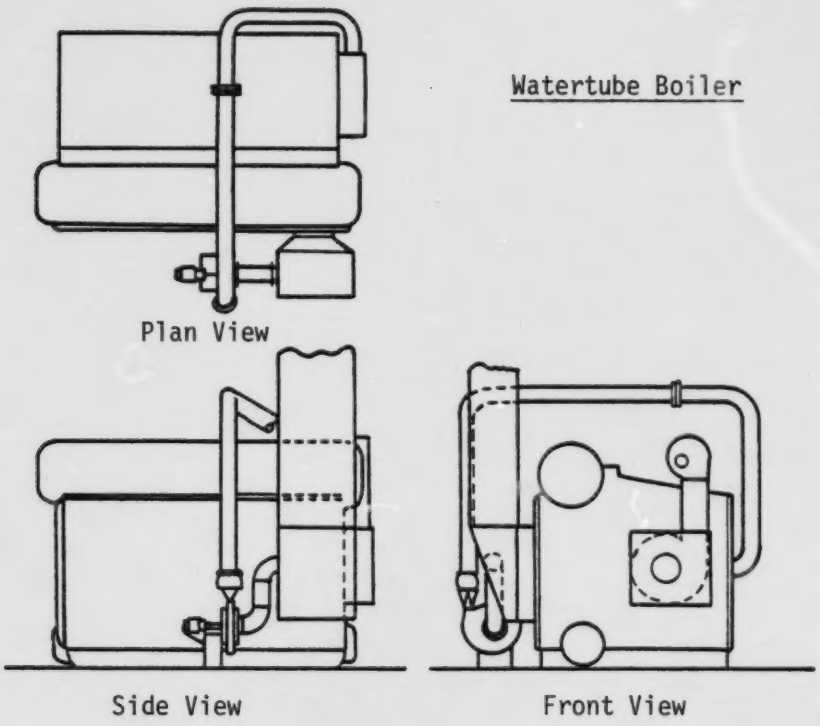
Space Conditioning Inc.
Harrisburg, Virginia

Todd-CEA Inc.
New York, New York

York-Shipley Inc.
York, Pennsylvania

John Zink Company
Tulsa, Oklahoma

Zurn Industries, Inc.
Erie City Energy Division
Erie, Pennsylvania



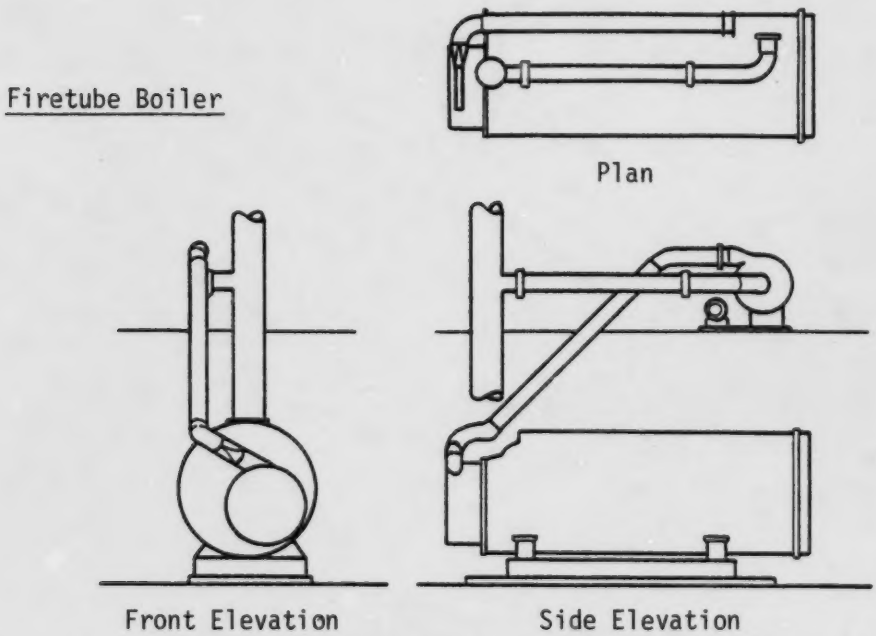


Figure 2-3. General layout of a watertube and a firetube boiler with flue gas recirculation.

Cast iron boilers in industrial services are generally used for space heating. They are usually square or rectangular and consist of several vertical sections. Water enters each section at the bottom and the steam or hot water exits from the top. In each section, the combustion gases pass through a maze of tubes. These tubes transfer heat from the gas to the water. The capacity of the commercial cast iron boiler is determined by the number of sections.

Cast iron boilers are reliable, with an average boiler life of about 50 years. They require little maintenance and can handle overloading or demand surges. The major problem associated with cast iron boilers is that the sections tend to deform, which may cause flue gases to leak from the joints. The manufacturers of cast iron boilers in the United States are listed in Table 2-4.

For further descriptions of the various types of industrial boilers the reader is referred to the references at the end of this section.

2.2 Current Industrial Boiler Inventory

Most inventories of industrial boilers also include commercial boilers. The total number of industrial and commercial boilers in service in 1977 is estimated to be about 1,800,000. The total firing capacity of these boilers is about 4,500,000 x 10^6 Btu/hr. Less than 1 percent of the boilers exceed the existing NSPS limiting size of 250 x 10^6 Btu/hr, but they represent 17 percent of the installed capacity. About 72 percent of these boilers are classified as commercial and are used primarily for space heating in commercial and institutional buildings. The other 28 percent are classified as industrial boilers and are used primarily for generating process steam and for space heating. Figure 2-4 shows the distribution of commercial nd industrial boilers by design type. Although the absolute number of commercial boilers is greater, the industrial boilers are generally much larger. Consequently, industrial boilers represent 69 percent of the total firing capacity.

TABLE 2-4. CAST IRON BOILER MANUFACTURERS

American Standard Inc., Industrial Division Detroit, Michigan
Burnham Corp., Heating and Cooling Division Irvington, New York
Crane Company Chicago, Illinoia
Dunkirk Radiator Corporation Dunkirk, New York
Hydrotherm, Inc. Northvale, New Jersey
Peerless Heater Company Boyertown, Pennsylvania
H. B. Smith Co., Inc. Westfield, Massachusetts
Utica Radiator Corporation Utica, New York
Weil-McClain Company, Hydronic Division Michigan City, Indiana

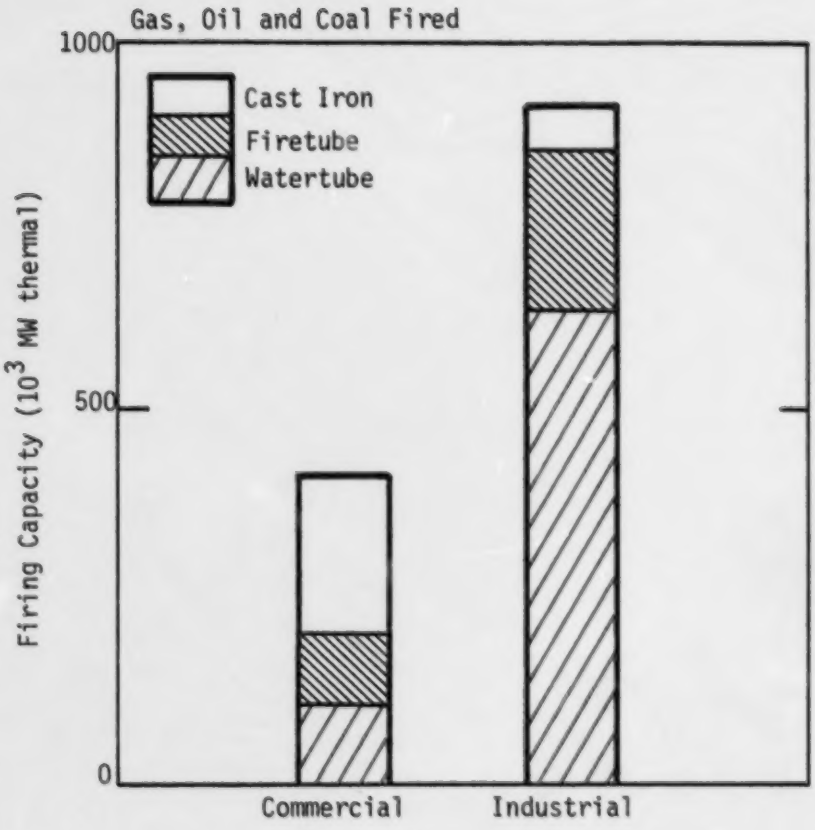


Figure 2-4. Distribution of commercial and industrial boiler capacity by type[2.3].

Figure 2-5 presents data collected by Locklin et al.[2.2] and shows the population breakdown of industrial boilers installed in 1972 by boiler type and capacity. The Scotch firetube boiler is the most popular package boiler in the small size range, but is not available in sizes greater than a firing rate of 25 x 10^6 Btu/hr. Above this capacity all package boilers are watertubes. Figure 2-6 compares the fuel capability of the industrial boiler population. For existing boilers the most popular fuels are natural gas and fuel oil. However, recent boiler sales indicate that there is an increasing trend towards duel-fuel capability. As natural gas supplies become restricted more industrial consumers will be required to accept natural gas on an interruptable basis, thus necessitating duel-fuel capability for industrial boilers.

Figure 2-7 shows the number and aggregate capacity of distillate and residual oil-fired industrial boilers organized by boiler design. Note that the number of boilers fired with residual oil is approximately twice as great as the number fired with distillate oil. The residual oil-fired boilers are generally larger and as a result they account for approximately five times the aggregate capacity as the distillate oil-fired boilers.

Cast iron boilers represent about half of the total number of boilers in service. However, due to their small capacity, the aggregate capacity of the cast iron boilers is insignificant. Thus, cast iron boilers do not consume a significant portion of distillate or residual oil. Firetube boilers number about the same as cast iron boilers. However, due to their much larger average capacity, the aggregate capacity of firetube boilers is many times greater than cast iron boilers. Watertube boilers are smallest in number but account for over half of the aggregate capacity due to their generally larger size.

The distribution of cast iron, firetube and watertube boilers by boiler capacity is shown in Figure 2-8 for distillate oil and residual oil. These figures clearly show the size variations discussed previously. The majority of the cast iron boilers have capacities less than 400 x 10^3 Btu/hr. These small units are primarily used for space heat in small industrial

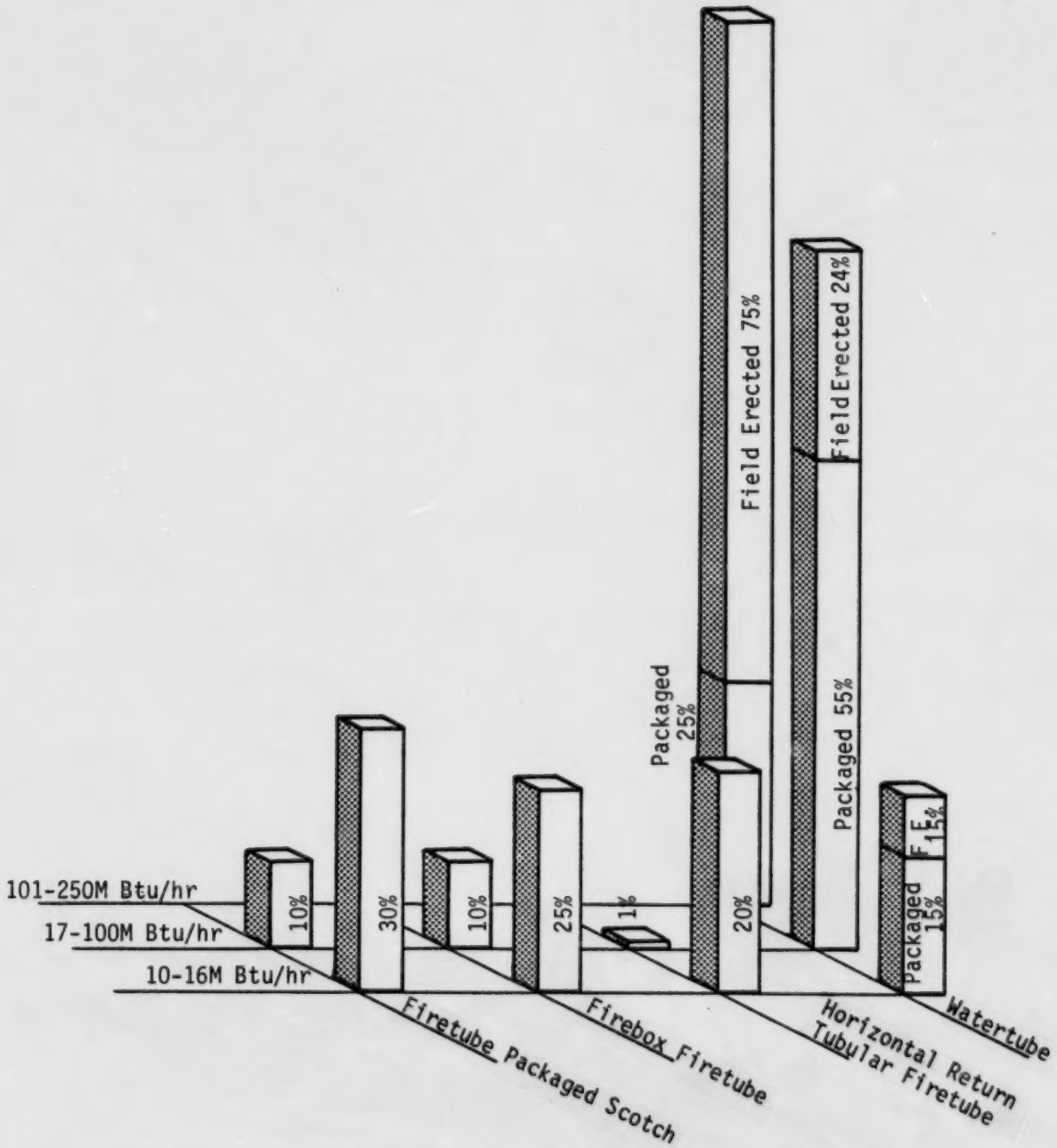


Figure 2-5. Population breakdown of industrial boilers by design type and capacity[2.2].

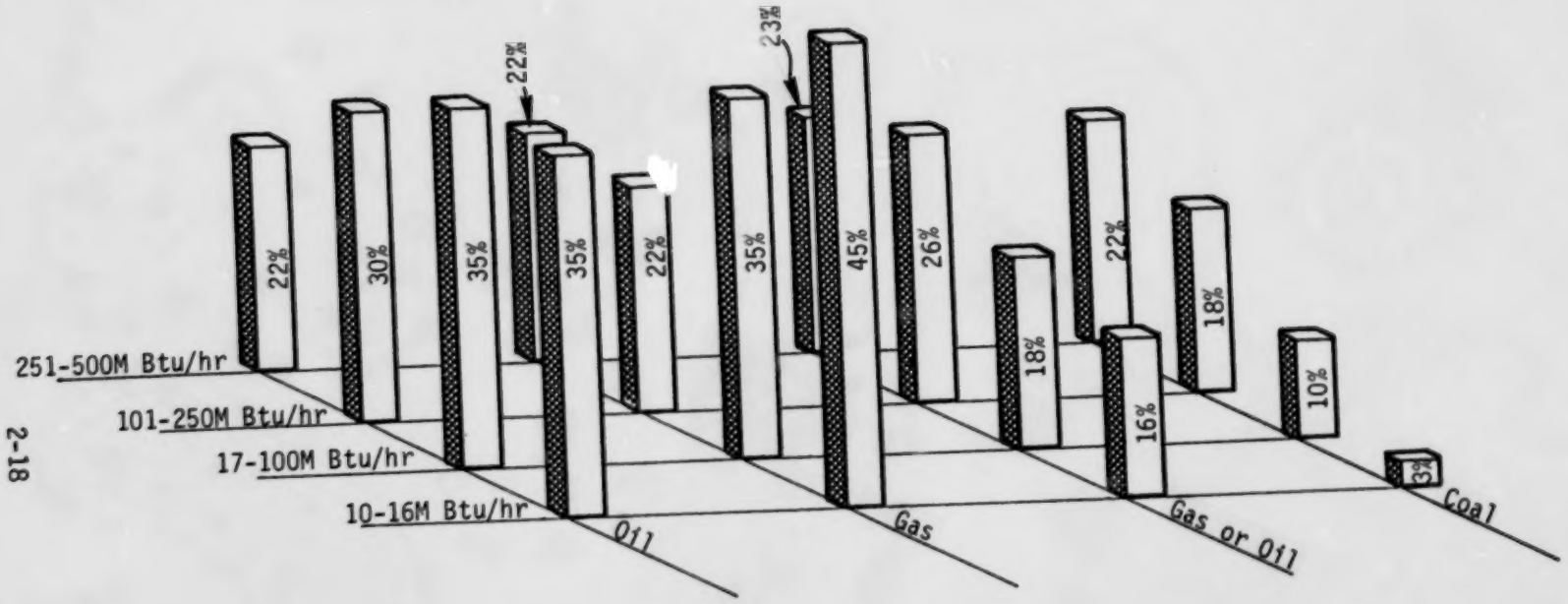


Figure 2-6. Population breakdown of industrial boilers by fuel capability and capacity[2.2].

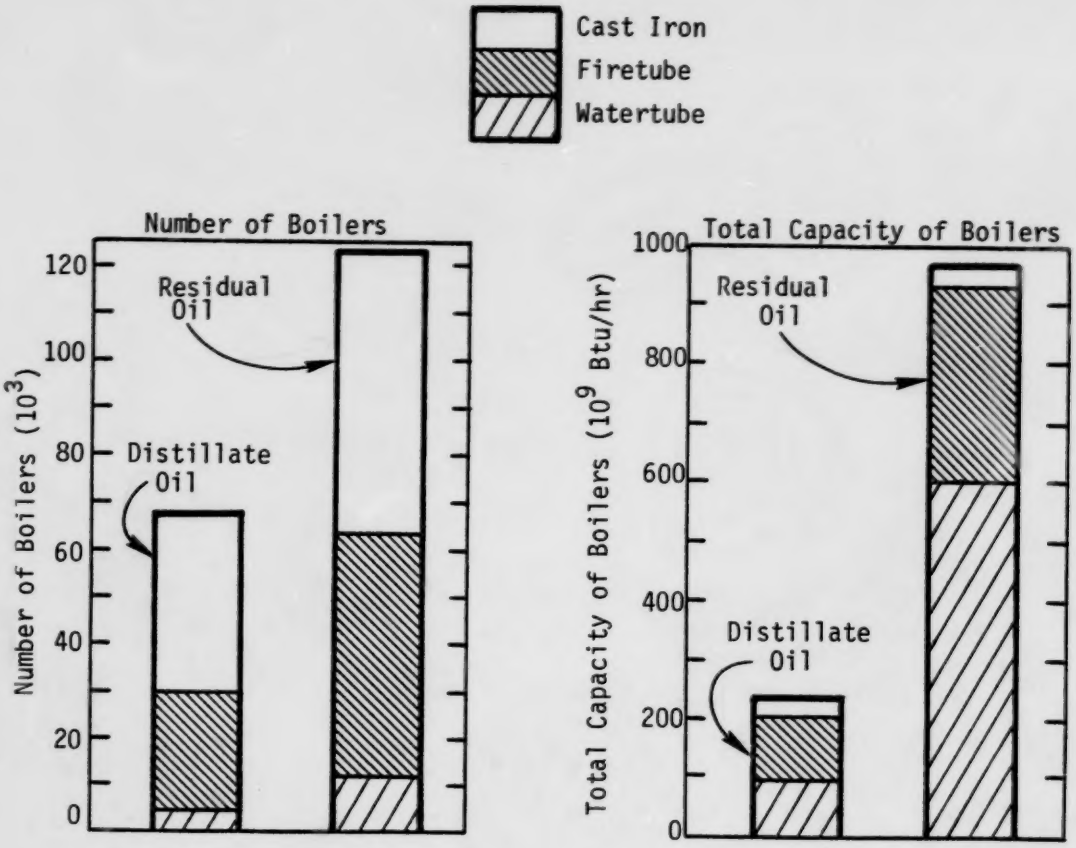
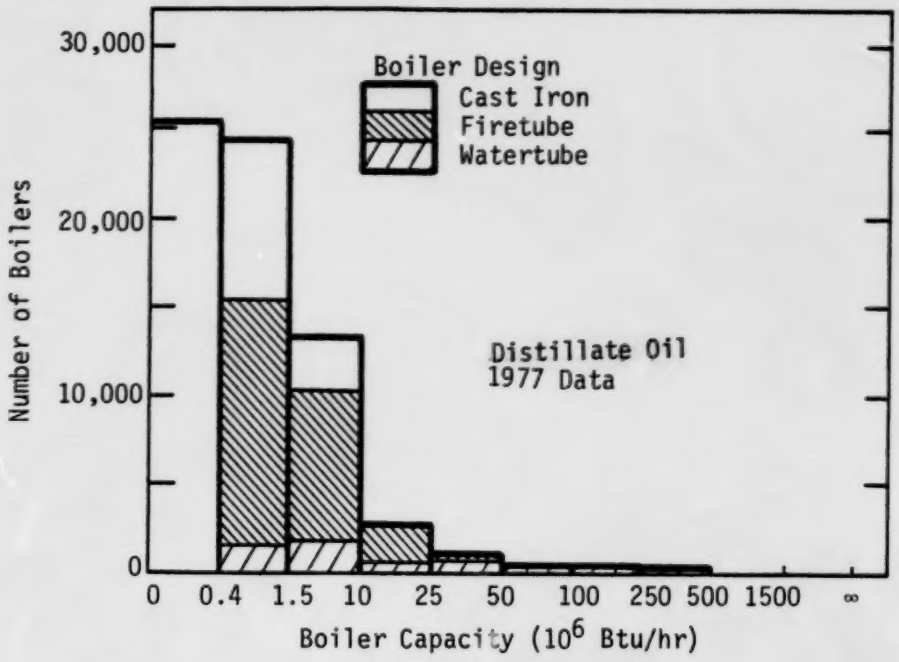


Figure 2-7. Total number and capacity of industrial boilers[2.3].



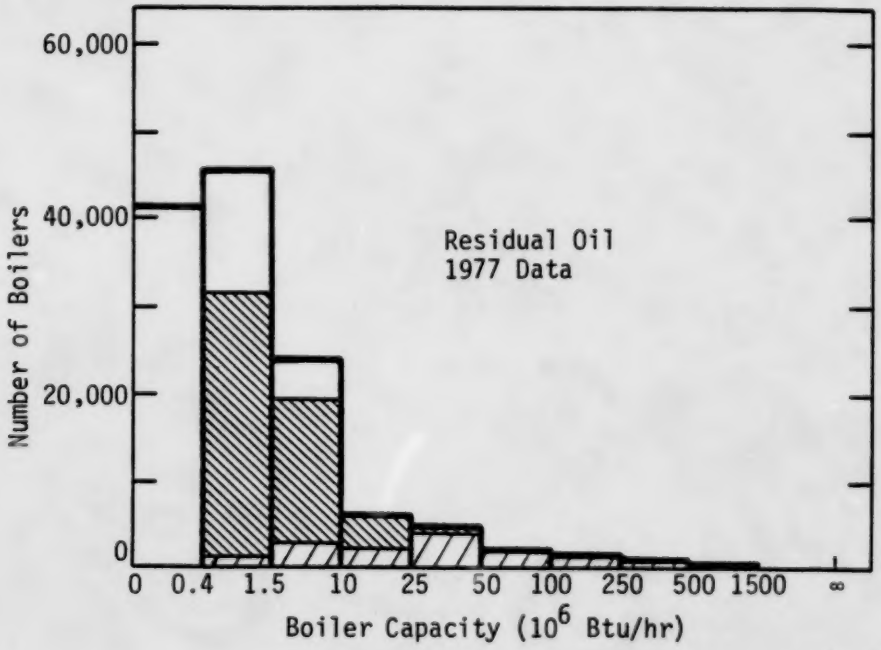


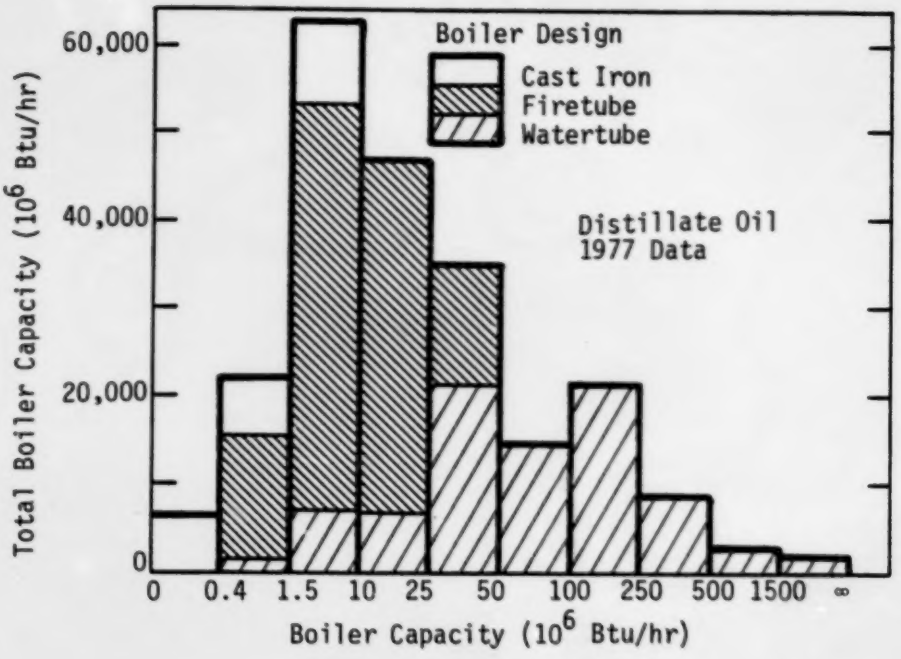
Figure 2-8. Total number of boilers versus capacity[2.3].

installations. Thus their operation is primarily seasonal and the overall utilization factor is low. Most of the firetube boilers have capacities of about 1.0×10^6 Btu/hr. However, the largest firetube boilers range up to about 50×10^6 Btu/hr. Distillate oil-fired watertube boilers are concentrated in the 0.4 to 10×10^6 Btu/hr range. However, the residual oil-fired watertube boilers average 25 to 50×10^6 Btu/hr.

The aggregate capacity of cast iron, firetube, and watertube boilers by boiler capacity is shown in Figure 2-9 for distillate oil and residual oil. As expected, these data show that the cast iron boilers are insignificant in each size range except for 0.0 to 0.4×10^6 Btu/hr. Firetube boilers account for the majority of boiler capacity in the 0.4 to 25×10^6 Btu/hr range. Note, however, that the watertube boilers are approximately evenly distributed from 25 to 250×10^6 Btu/hr and this capacity range accounts for approximately 2/3 of the aggregate watertube boiler capacity.

Figure 2-10, taken from the work of Locklin et al.[2.2] shows past and predicted trends in package boiler population for 10 to 16 thousand lb steam/hr and 17 to 100 thousand lb steam/hr, respectively. The statistical information available to Locklin suggests that the fraction of installed capacity attributable to packaged Scotch firetube boilers will increase through 1990. Thus, the development of a low emission combustion system for this type of boiler is of considerable interest for the future.

Figure 2-11 illustrates the future fuel usage trend and emphasizes the need for dual fuel-fired systems for firetube package boilers. It is estimated that by 1990, less than 10 percent of the total installed capacity in the size range of interest will be solely gas-fired and that most units will be dual fuel-fired (oil and gas). It is very probable that in heavily populated areas gas will be supplied on an interruptible basis and during the heating season virtually all package boilers will burn liquid fuels.



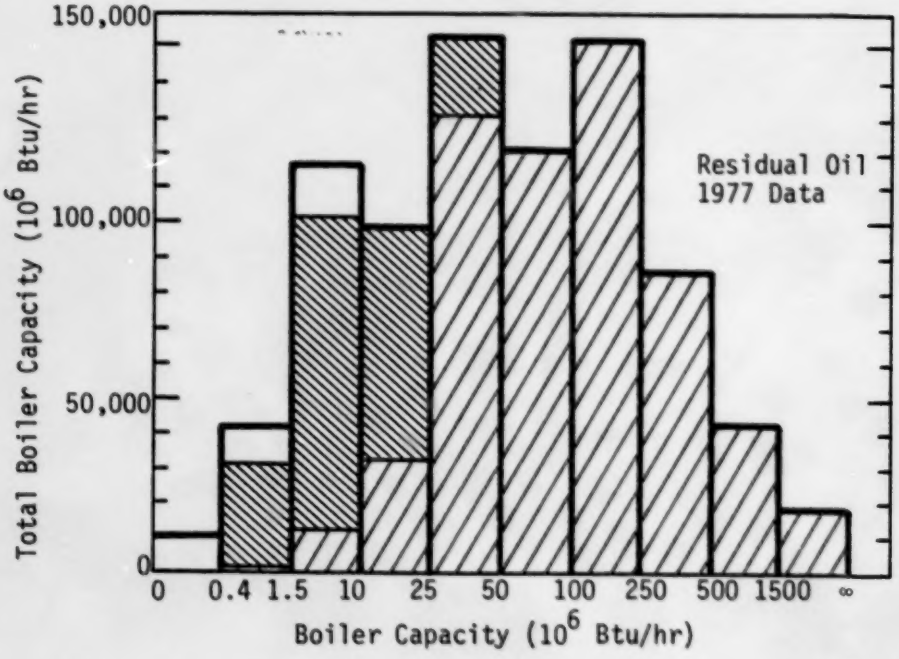
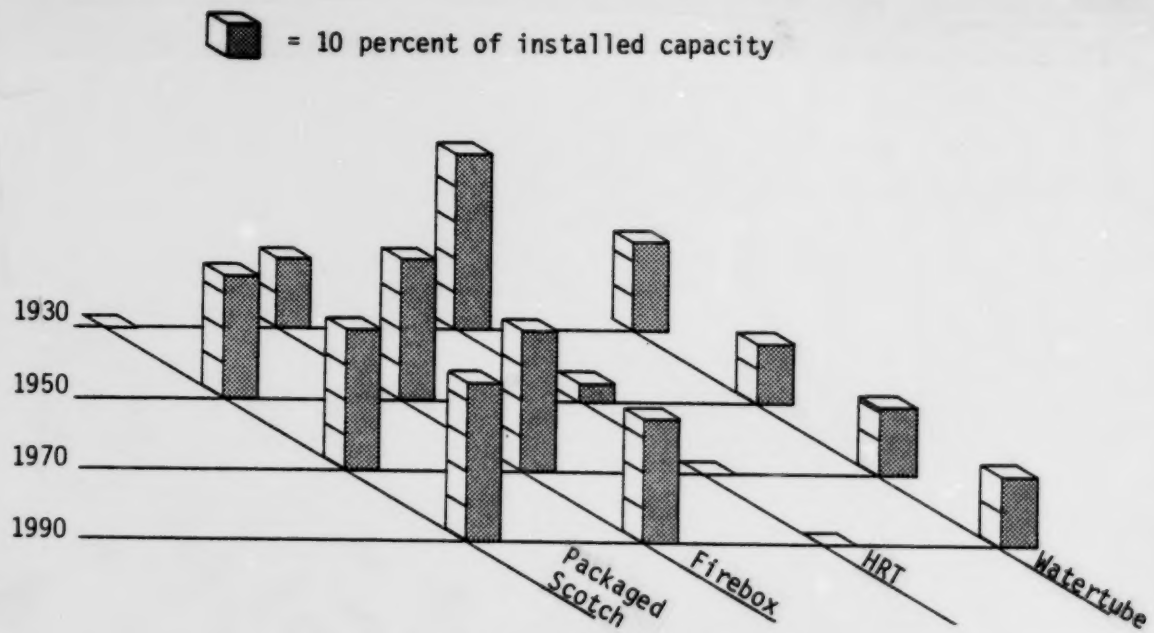
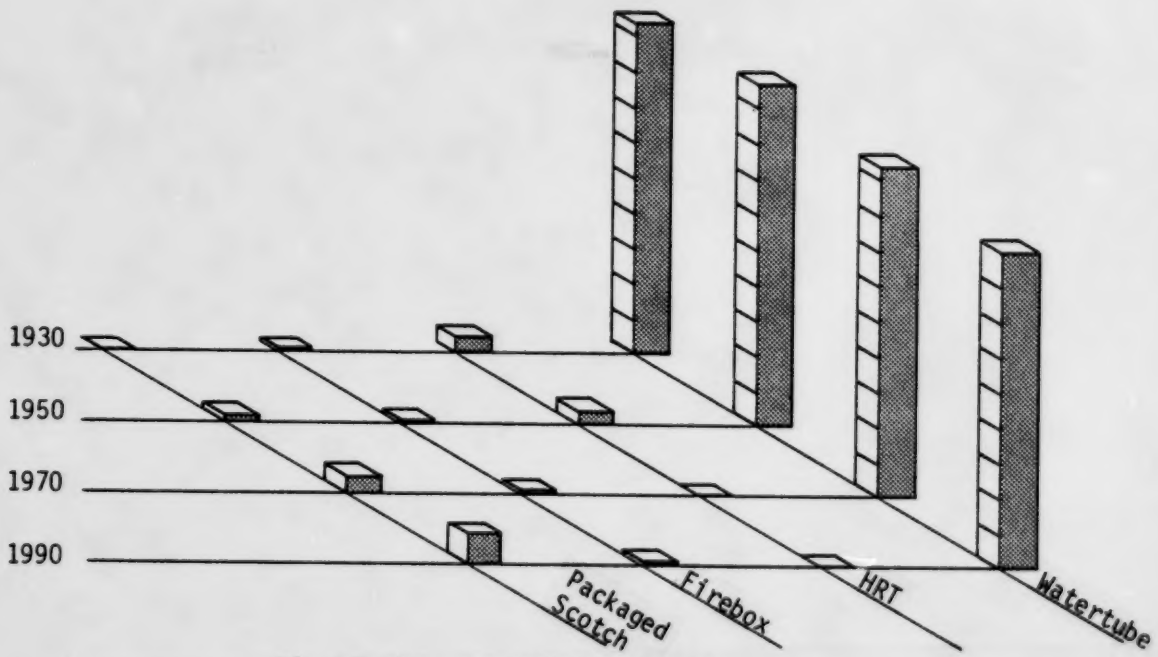


Figure 2-9. Total capacity of boilers versus capacity[2.3].

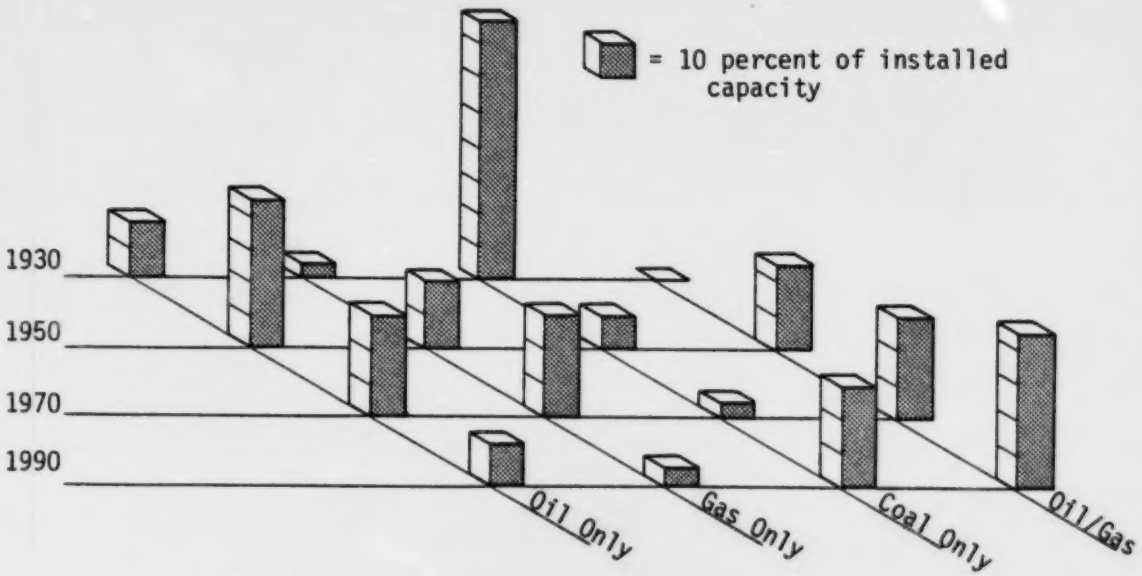


a) 10,000 - 16,000 lb steam/hr

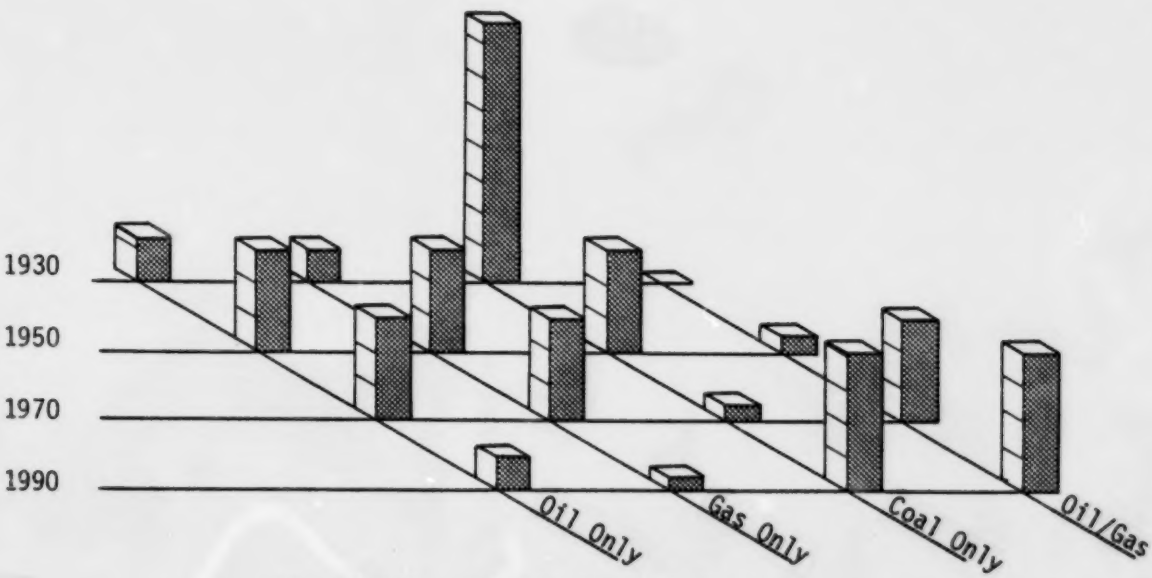


b) 17,000 - 100,000 lb steam/hr

Figure 2-10. Past and predicted trends in package boiler population, (percentage of installed capacity)(2.2).



a) 10,000 - 16,000 lb steam/hr



b) 17,000 - 100,000 lb steam/hr

Figure 2-11. Past and predicted trends in package boiler firing (percentage of installed capacity)[2.2].

2.3 Package Boiler Oil Burners

Burners which are currently available for industrial boilers have traditionally been designed to burn oil in the most efficient manner for the particular application. Rather than minimizing pollutant emissions, the design requirements for oil burners have been based upon:

- Stability. Flame stability is of paramount importance since it is a requirement closely linked to safety. Stability may be considered as an ignition phenomena, i.e., the ignition zone is anchored close to the fuel injector and remains stable with time. Instabilities are also encountered in boilers where combustion-driven oscillations produce excessive noise or pressure fluctuations within the combustion chamber.

- Ignition. Burner design must provide for rapid, safe ignition of the fuel/air mixture is a cold furnace. Ignition systems should be designed to have a long lifetime, be easily replaced and inexpensive. Ignition may be accomplished by spark discharge directly or by the use of a pilot flame.

- Turndown Capability. The burner must be capable of operating over a wide range of firing rates. A package boiler will typically require at least a 3 to 1 turndown ratio, and may be fully modulated so that the fuel flow will follow the steam demand. Burner performance must be maintained over a wide load range as well as during load changes. Many firetube boilers operate on a high/low firing cycle making their design easier.

- Flame Shape. The flame shape obtained from the mixing condition produced by the burner depends on the particular combustion chamber geometry. Flame patterns and heat release characteristics are matched to the configurations of the combustion chamber. Impingement of the fuel on any surface is avoided as it may form coke deposits which may further interfere with flame development

and possibly affect thermal efficiency by increasing unburned carbon.

- Mechanical Construction. Burner life cycle costs for package boilers are relatively low, and thus, the burner should be of simple design and easy to produce.

- Control. The burner controls must provide for safe startup, normal running and shutdown of the burner, as well as follow the operational requirements (e.g., load swings) of the boiler.

Most package boiler burners operate at between 15 and 25 percent excess air (3 to 5 percent stack oxygen) in order to produce a clean, bright flame which provides very low smoke emissions. Recent trends in burner design have been toward low excess air designs in order to increase overall boiler efficiency by reducing stack losses. These low excess air burners typically operate between 5 and 10 percent excess air (1 to 2 percent oxygen). Low excess air burners tend to produce lower NO_x emissions than conventional burners and therefore are sometimes fitted as a method of NO_x control.

In simple terms, a package boiler burner consists of a fuel-oil nozzle to atomize the liquid fuel, a burner throat to provide the desired distribution of angular and tangential air velocity, stabilization vanes, and in many instances, a refractory burner exit. Figure 2-12 shows two typical burner systems for firetube boilers. Firetube boilers are typically fired by a single burner, and usually have an integral fan/windbox arrangement since air preheat is not generally available. Firetube furnaces require a flame with a relatively high L/D and therefore there usually is not a high level of swirl applied to the combustion air. Flame stability is achieved by the use of "diffuser" plates or vanes which impart turbulence and recirculation near the fuel injector without causing the flame to "bush out" and impinge on the furnace walls.

Figure 2-13 shows two typical burner arrangements for watertube boilers. The furnace of a watertube boiler has a much shorter L/D than firetube

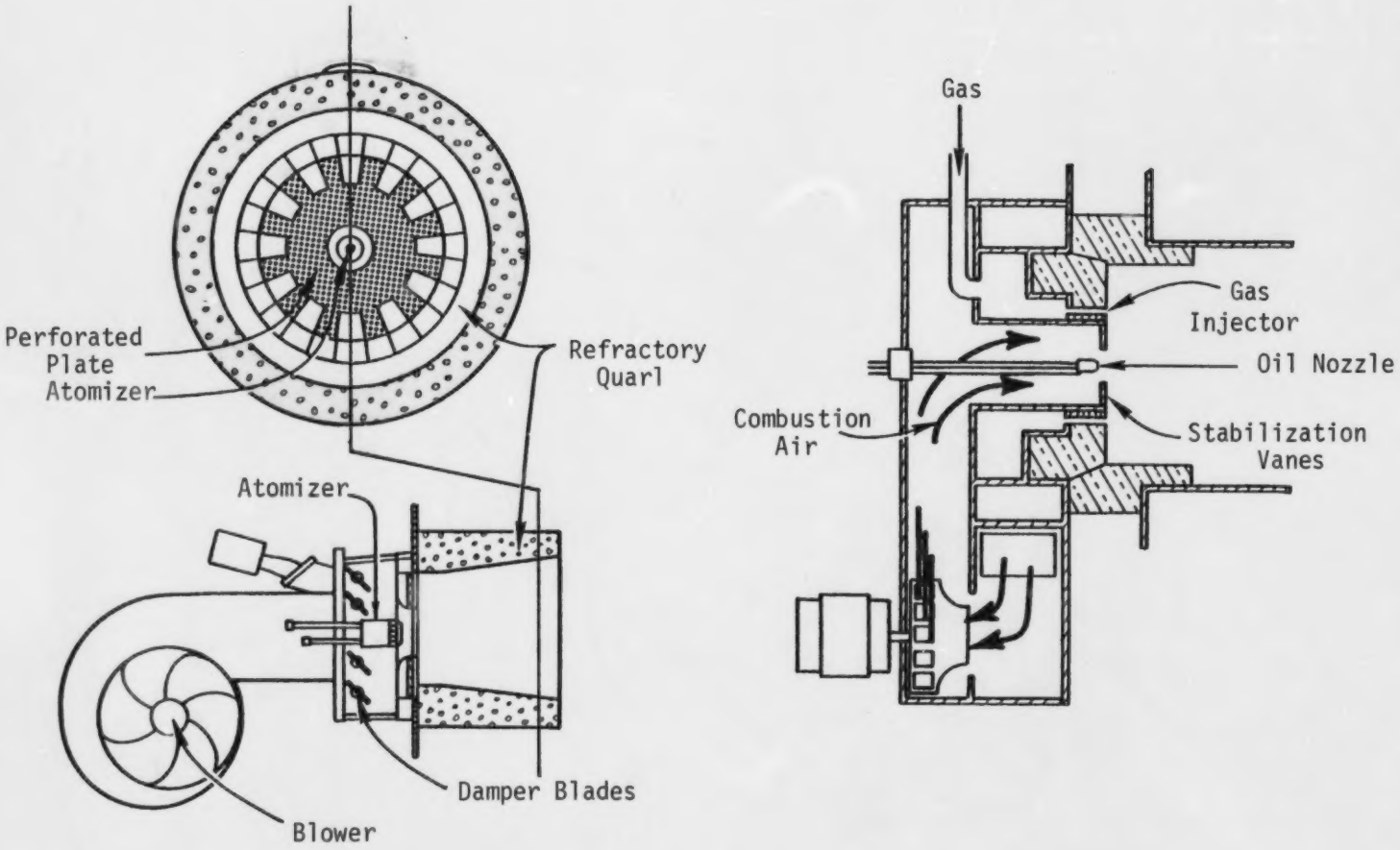


Figure 2-12. Typical firetube boiler burners.

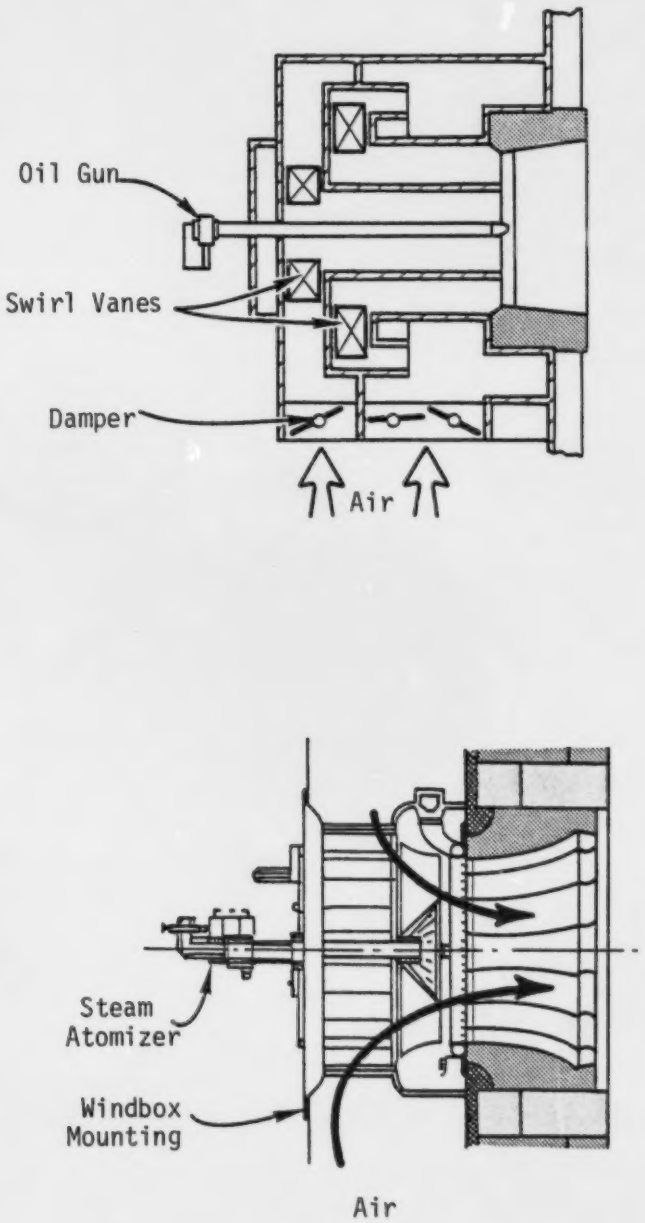


Figure 2-13. Typical burners for package watertube boilers.

boilers and as such requires much shorter, wider flame shape. Watertube boilers are normally fired by register burners which are capable of imparting a variable level of swirl to the combustion air. Swirl is varied to match the flame shape to the combustion chamber and to maintain flame stability at high turndown. Some burners are designed with an integral fan/windbox assembly as with firetube boilers; however, larger capacity watertube boilers may utilize air preheaters and multiple burners, so most watertube burners are designed to be mounted independent of the combustion air supply.

Typical low-excess air oil burners for watertube boilers are shown in Figure 2-14. These burners tend to provide more intense mixing of the flame due to higher throat velocities (smaller throat diameters) and oil gun-mounted swirlers. The burners shown in the figure do not have variable air registers. Flame stability is achieved through design of the swirler vane assembly.

Flame shaping is achieved by variation of axial and tangential momentum imparted to the combustion air, design of the atomizer, and shape of the burner quarl (divergent exit). Figure 2-15 shows flow patterns obtained in a furnace without flame using a research burner[2.4], Increasing swirl level and increased divergent exit angle led to more rapid expansion of the air flow and eventually induced a central recirculation zone along the burner axis. Observations with flame confirmed similar trends. The final configuration for a particular boiler furnace is generally arrived at empirically based on experience with many boiler/burner configurations.

Oil atomizers commonly used in package boilers fall into four categories: air-assist, steam-assist, mechanical, and rotary. Examples of these four atomizer types are shown in Figure 2-16. There is a wide variation in particular configuration among the four classes. Each burner manufacturer chooses a configuration designed to give optimum performance with their own burner throat configuration.

Mechanical atomizers are used widely for distillate oil only. Air or steam assist atomizers are generally used with heavy residual fuels. Figure

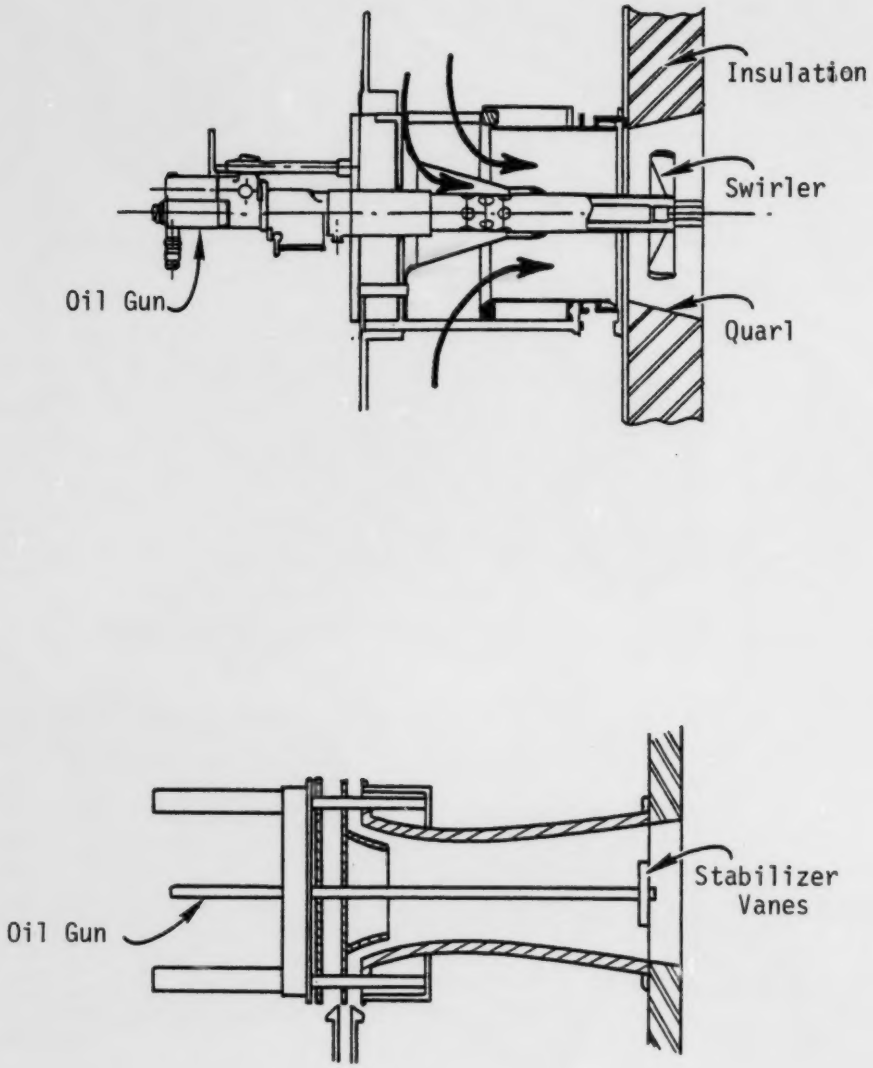


Figure 2-14. Typical "axial flow" low excess air watertube boiler burners.

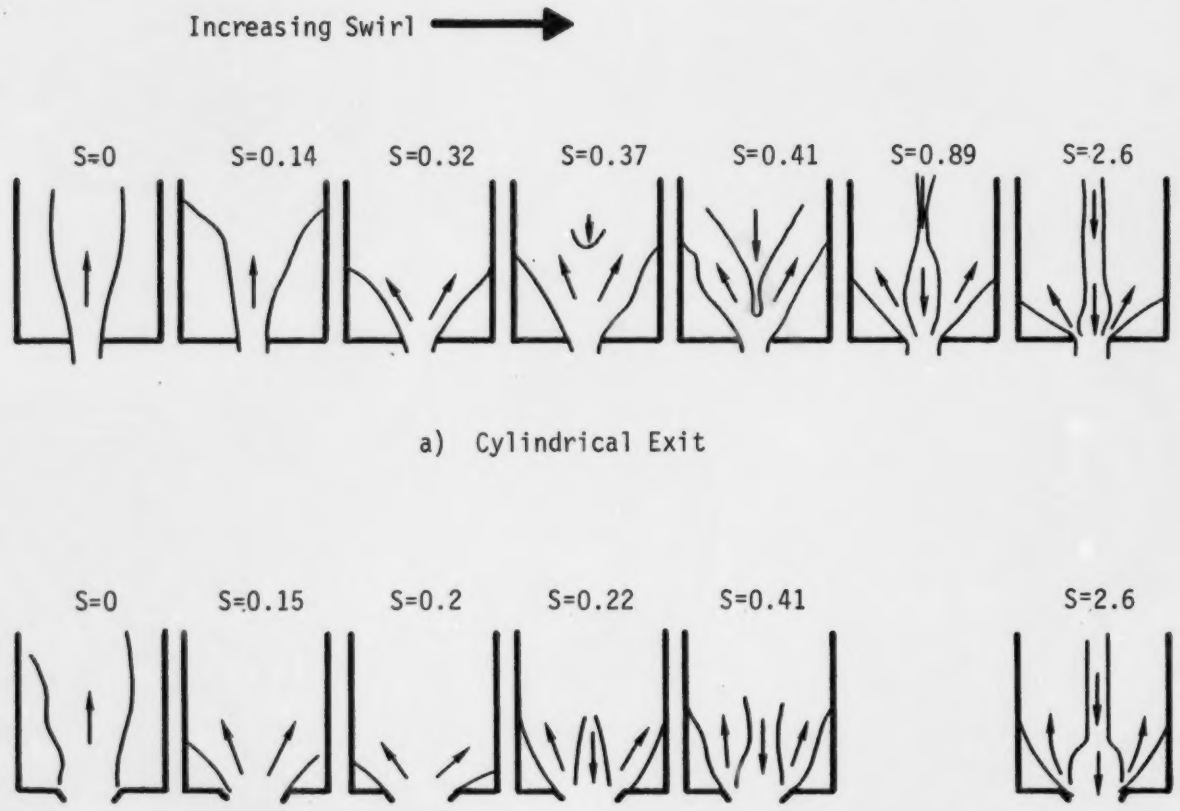
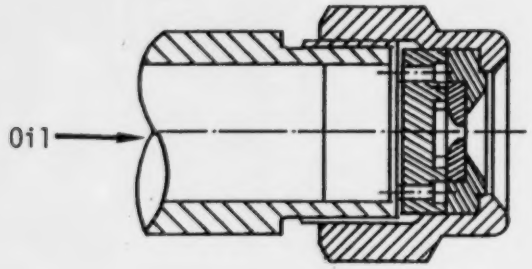
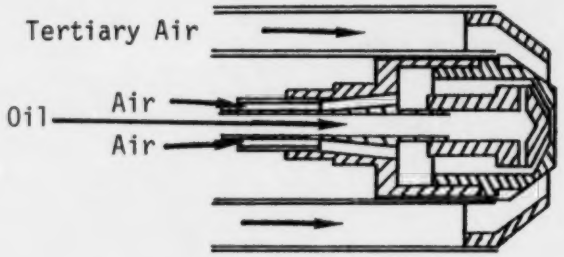


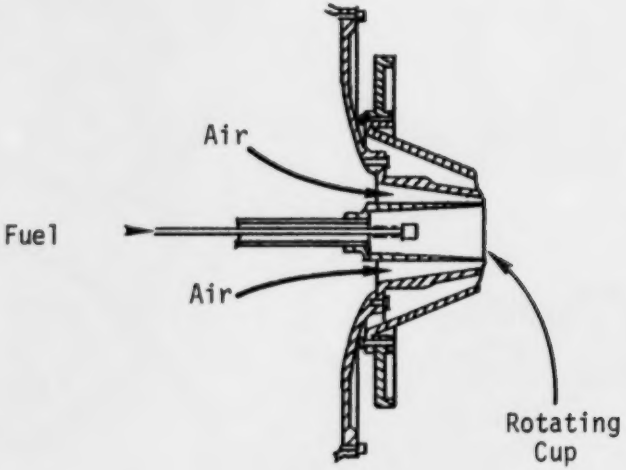
Figure 2-15. Cold flow patterns in a furnace as a function of swirl level (S = dimensionless swirl number) for two burner exit geometries (no flame).



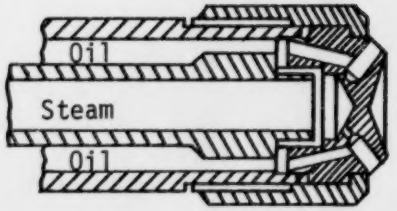
Mechanical Nozzle
(Pressure Jet Swirl Type)



Low Pressure Air Atomizing Nozzle



Rotary Atomizer



Steam-Atomizing Nozzle
(y-Jet Type)

Figure 2-16. Examples of oil atomizer types.

2-17 shows the distribution of oil atomizer types in the installed industrial boiler population. Air atomization is most prevalent in the smaller boiler capacities, but as size increases the use of steam atomizers dominates since steam is more readily available than air. The use of rotary atomizers is restricted to the smaller size range, and it is estimated that by 1990 they will be completely replaced by steam or air atomizers. Rotary atomizers provide stable ignition over a wide range of turndown; however, they are prone to excess particulate emissions.

In general, burner controls serve to provide safe startup and shutdown of the burner, safe normal running operation, and firing rate modulation to follow steam demand. Proper location of flame detectors so that unstable flames and false readings do not occur, for instance, is critical for safe burner operations. Firing rate modulation may be achieved either manually or automatically.

Figure 2-18 shows the main elements of a typical automatic boiler control system. There are usually several safety interlocks which must be satisfied before the ignition sequence starts. On starting the burner, the air blower starts and damper opens to purge remaining fuel from the furnace for a period of time ranging from a few seconds to several minutes, depending on the particular system. The ignition sequence then begins, providing safety interlocks are satisfied. After ignition, the firing rate control may be modulated between pre-set low-fire and high-fire conditions according to steam demand. Often burners are operated in an on/off mode at high-fire or low-fire to follow load demand. On shutdown, the controls typically return the burner to low fire, cut off the fuel flow, and again purge the boiler before finally turning off the air flow.

2.4 NO_x Control Techniques for Package Boilers

NO_x emissions from boilers can be reduced by several techniques:

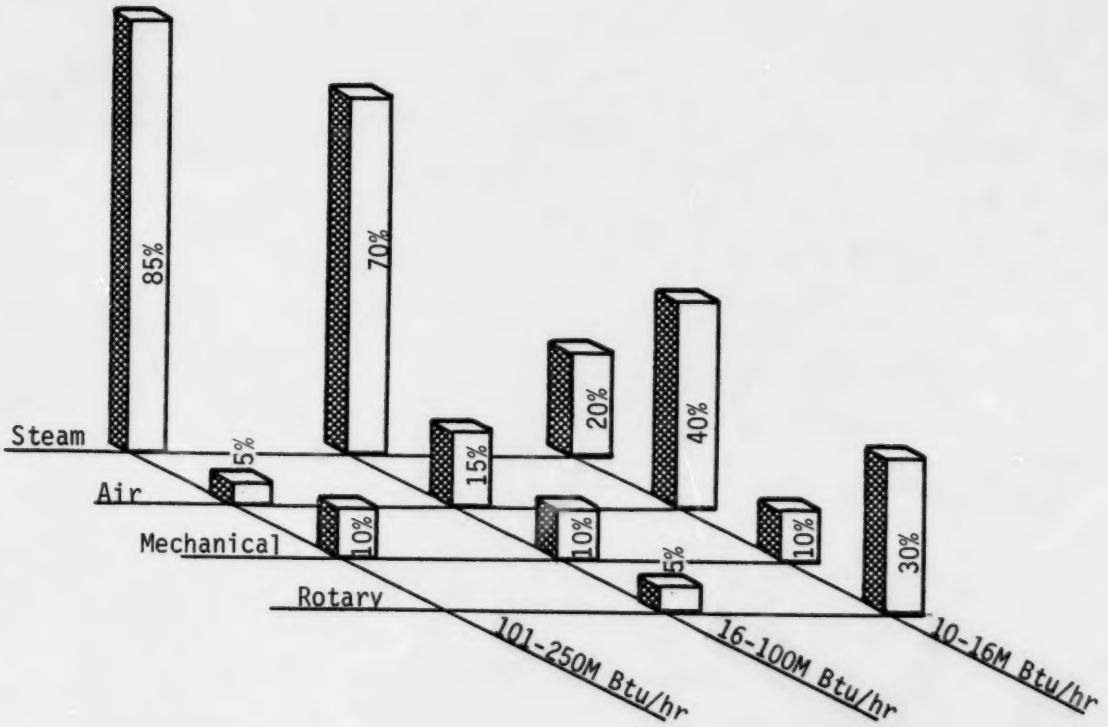


Figure 2-17. Population breakdown of industrial boilers by oil atomization method[2.2].

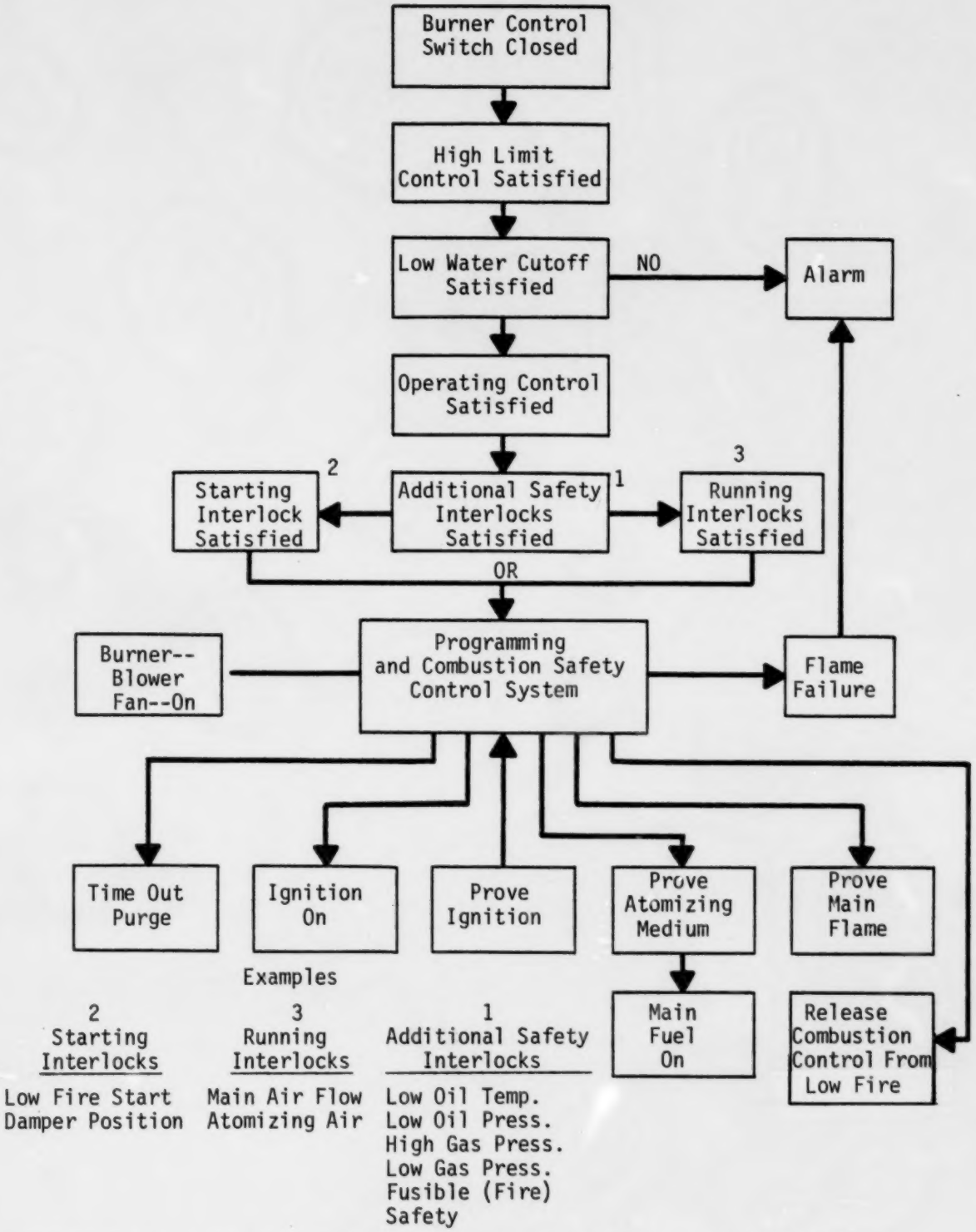


Figure 2-18. Typical safety control system for packaged firetube boilers (courtesy of the American Boiler Manufacturers Association).

- Fuel Switching or Blending. The boiler fuel can be changed from a high nitrogen to a low nitrogen fuel, thus reducing the amount of fuel NO produced.

- Low Excess Air Firing. In general, reducing excess air to a point just above the onset of smoke and CO emissions will result in lower NO_x emissions by restricting oxygen availability.

- Flue Gas Recirculation (FGR). Cooled combustion products are added to the combustion air to lower peak flame temperatures.

- Staged Combustion. The combustion air is divided into two streams, one of which is injected some distance from the burner throat, thus providing an initial fuel-rich section. This serves to minimize fuel NO conversion and with interstage heat removal prior to the addition of the secondary air, thermal NO production is minimized.

- Low NO_x Burners (Burner Design). The air and fuel injection systems can be designed in such a way as to reduce both fuel NO and thermal NO production by delaying fuel/air mixing and/or recirculation of combustion products.

One reason for changing the fuel in a package boiler would be to switch to a fuel with a lower adiabatic flame temperature, thus minimizing thermal NO production. Figure 2-19 shows the influence of both fuel type and excess air on emissions of NO_x from a firetube and watertube boiler respectively. Neither natural gas nor methanol contain fuel nitrogen compounds. Thus, thermal NO_x accounts for the total emissions from these fuels. The No. 5 fuel oil contained approximately 0.1 percent nitrogen, thus accounting for the higher emissions with that fuel. The difference in emissions between the two boiler types is attributed to variations in volumetric heat release rate, and therefore, bulk gas temperatures.

The addition of cooled combustion products (FGR) to the combustion air supply is known to be an effective method of controlling thermal NO_x

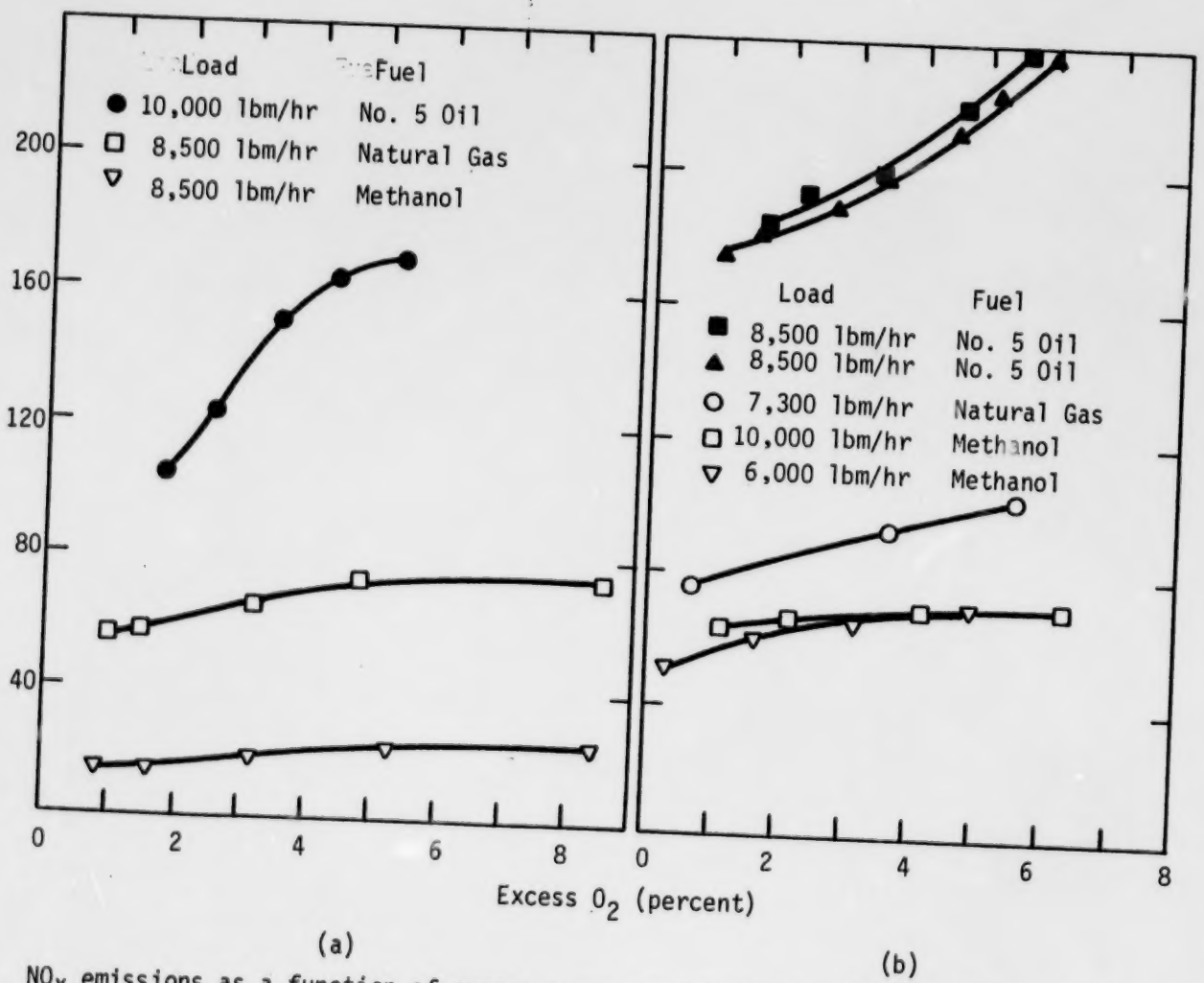


Figure 2-19. NO_x emissions as a function of excess oxygen and fuel type for (a) firetube boiler and (b) watertube boiler.

production. Figures 2-20 and 2-21 shows the effect of flue gas recirculation on NO_x emissions from a variety of combustion systems with nitrogen-free fuels and with residual fuel oil, respectively. It can be seen how much more effective flue gas recirculation is in controlling NO_x emissions when the fuel does not contain bound nitrogen. This result is not surprising since fundamental studies show fuel nitrogen conversion is not strongly dependent upon flame temperature. However, in real systems flame temperature might well have an effect upon the rate at which the fuel nitrogen compounds are evolved from liquid fuels.

Figure 2-22 shows results obtained by staging the combustion in a firetube package boiler with both natural gas and No. 5 fuel oil. The second stage air was injected downstream from the burner in the firetube from a series of injectors situated at the periphery of the combustion chamber. The axial location of these injectors could be varied. With the No. 5 fuel oil it can be seen that emissions are reduced by approximately 50 percent when the air through the burner corresponds to 90 percent of the stoichiometric air requirements. The increase in NO_x emissions with decreasing burner stoichiometry shown for natural gas firing can be attributed to two factors: (a) the low burner momentum under staged conditions which may inhibit fuel/air mixing close to the burner, and thus minimize the extent of reaction and therefore heat loss in the primary zone; and (b) the method of secondary air injection. If significant heat loss from the primary section has not taken place, high peak temperatures could be attained in the secondary zone because the mixing process may promote near-adiabatic peak temperatures as the overall equivalence ratio passes from fuel-rich to fuel-lean. These results indicate that caution should be exercised if staged combustion techniques are to be used with a dual-fuel burner.

Figure 2-23 compares the results of several investigations showing the reduction in NO_x as a function of burner stoichiometry for a variety of combustion systems and staging methods with nitrogen-free fuels. Two of the sets of experimental results presented in Figure 2-23 show that NO_x emissions actually increased under staged combustion conditions. Thus the results presented in Figure 2-22 do not represent an isolated incident. Figure 2-24

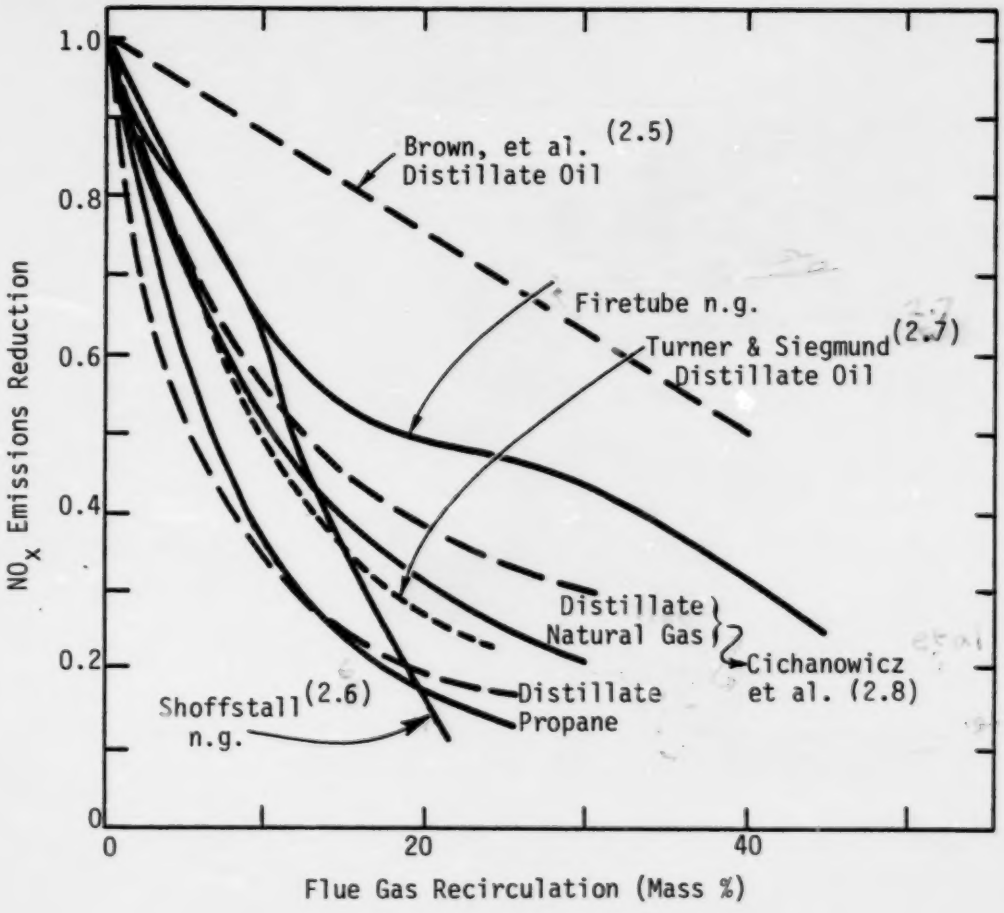


Figure 2-20. The effect of flue gas recirculation of NO_x emissions from nitrogen-free fuels for a variety of combustion systems.

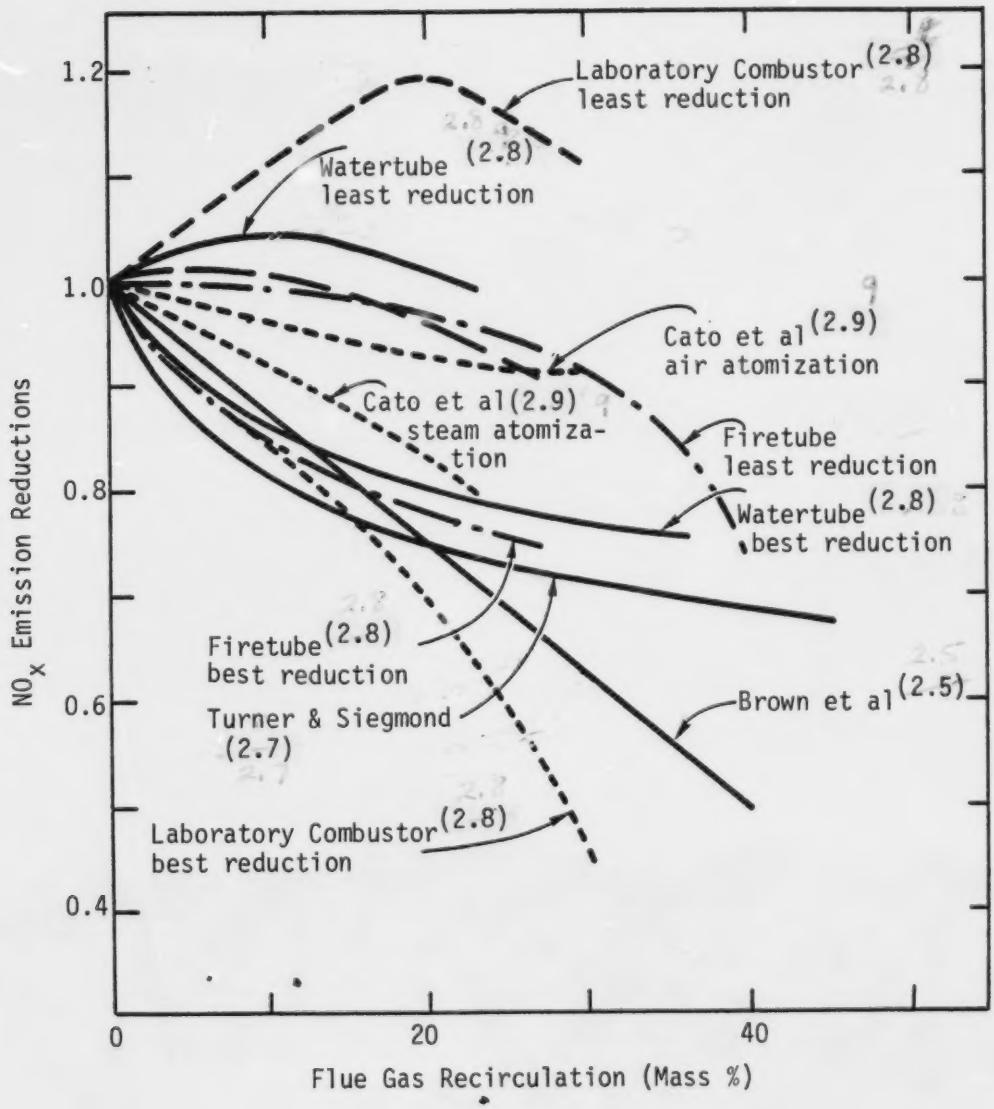
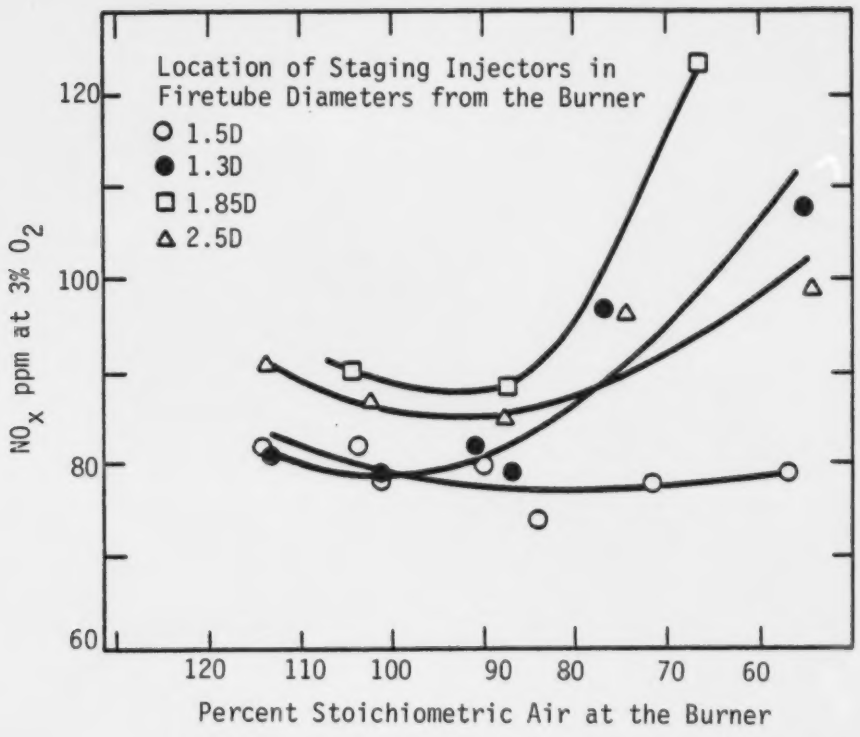


Figure 2-21. The effect of flue gas recirculation on NO_x emissions from residual fuel oil for a variety of combustion systems.

(a)



(b)

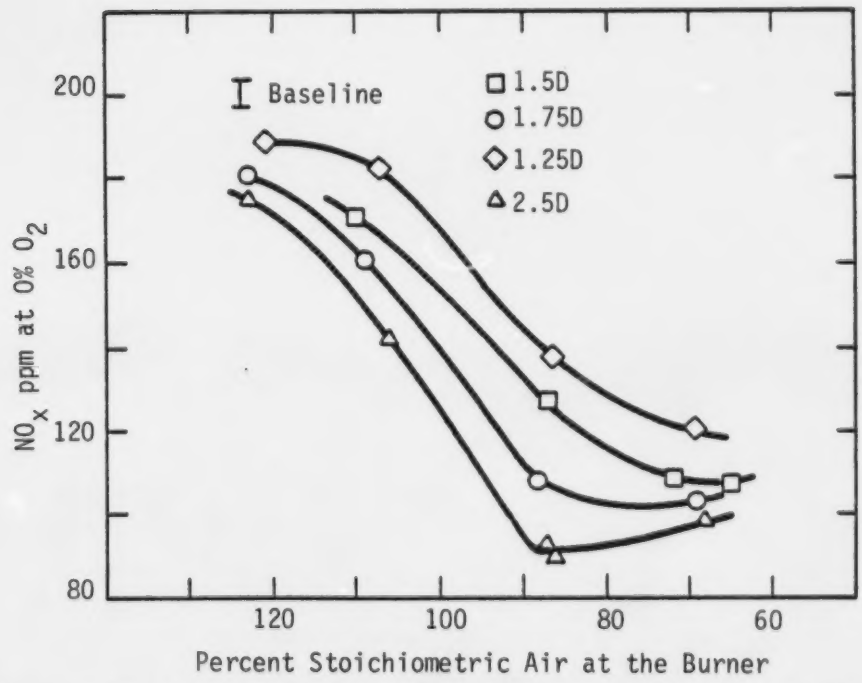


Figure 2-22. The influence of location of staged air injection on NO_x emissions from a firetube boiler burning (a) natural gas (2.9 percent O_2) and (b) No. 5 fuel oil (6,000 lbm/hr, O_2 = 4 percent ± 0.3).

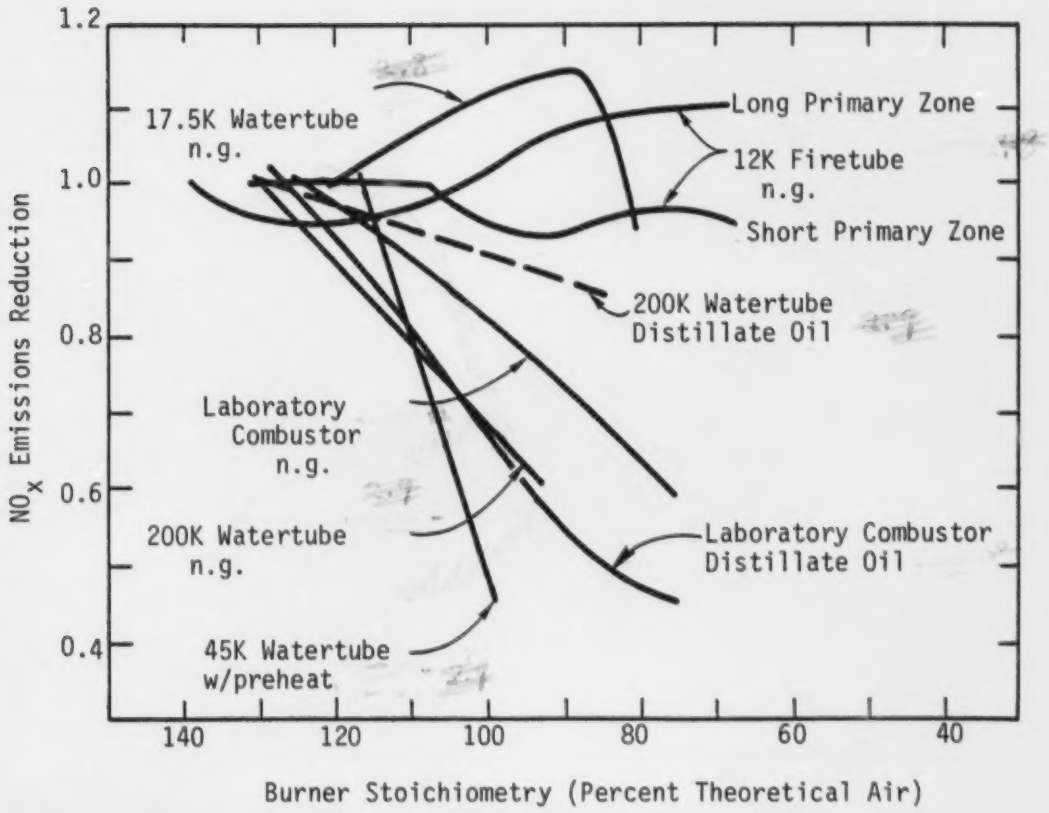


Figure 2-23. The effect of burner stoichiometry on NO_x emissions reduction for a variety of combustion staging systems.

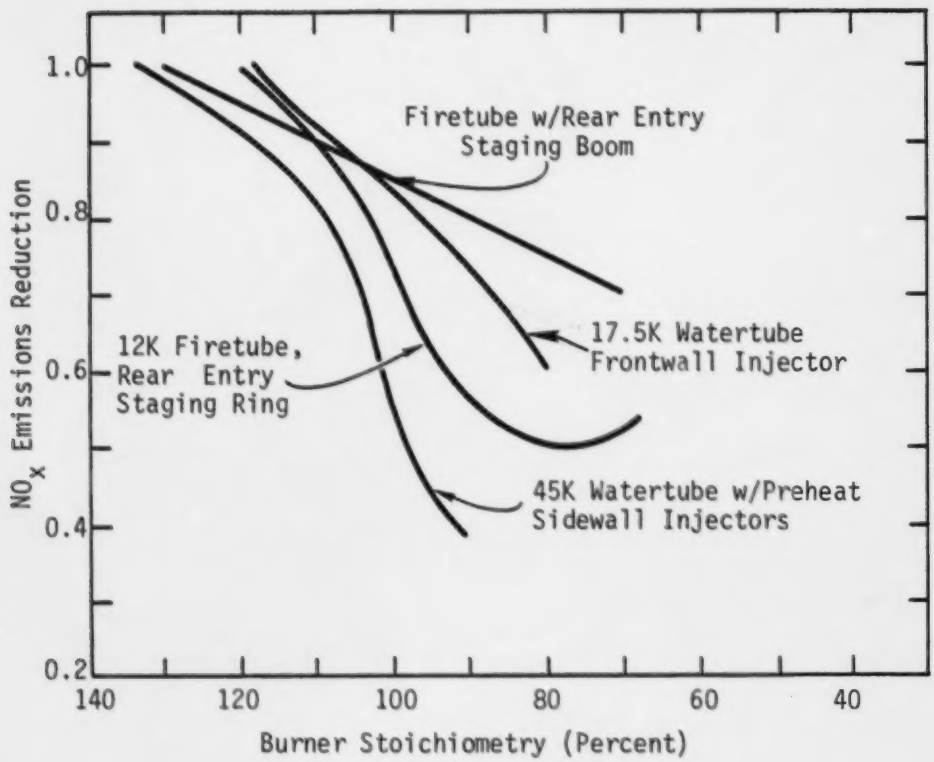


Figure 2-24. The effect of burner stoichiometry on NO_x emissions reduction from residual fuel oil for a variety of combustion staging systems.

compares several attempts at controlling NO_x emissions from fuels containing bound nitrogen. Turner and Siegmund[2.7] demonstrated substantial NO_x reduction with a 50 hp firetube boiler with remote air addition from a boom protruding into the combustion chamber from the rear of the boiler. However, these results were obtained at 40 percent of the burner design firing rate, and high pressure air was available for use in the secondary air injection system.

Low excess air firing can reduce NO_x emissions, although the minimum excess air level (therefore NO levels) which can be achieved is usually limited by the onset of smoke and CO emissions. In Figure 2-19, the greatest effect of excess air level was seen for the No. 5 fuel oil. Reduced excess air has the effect of reducing oxygen availability for oxidation of fixed nitrogen species in the burner zone, and thus can be most effective for nitrogen-containing fuels. Although low excess air burners can be an effective NO_x control technique for retrofit to industrial boilers for specific applications, in many cases they can produce higher NO_x emissions than conventional burners if they are not operated under low excess air conditions. This is especially true with nitrogen-free fuels such as natural gas and distillate oil (see Figure 2-23). Field test data for high-nitrogen fuel oil, shown in Figure 2-25, compares NO_x emissions from conventional and low excess air burners. At 1.0 percent O_2, the least squares fit to low excess air burner data results in 417 ppm. This level is achieved with a conventional burner at about 7.7 percent O_2. Thus if the low excess air burner is not operated at its minimum excess air operating point, NO_x emissions can be higher than conventional burners. In general, low excess air burners are not a reliable NO_x control retrofit for industrial boilers.

More advanced burner designs which can achieve much lower NO_x levels are currently under development in the U.S. for industrial boilers. The burners currently available usually apply either distributed fuel/air mixing concepts or internal recirculation. Distributed fuel/air mixing concept may involve the use of outboard (tertiary) air ports or multiple-jet atomizers. The range of low NO_x burners available for industrial boilers in the U.S. is quite limited in the absence of regulations to create a market. The widest

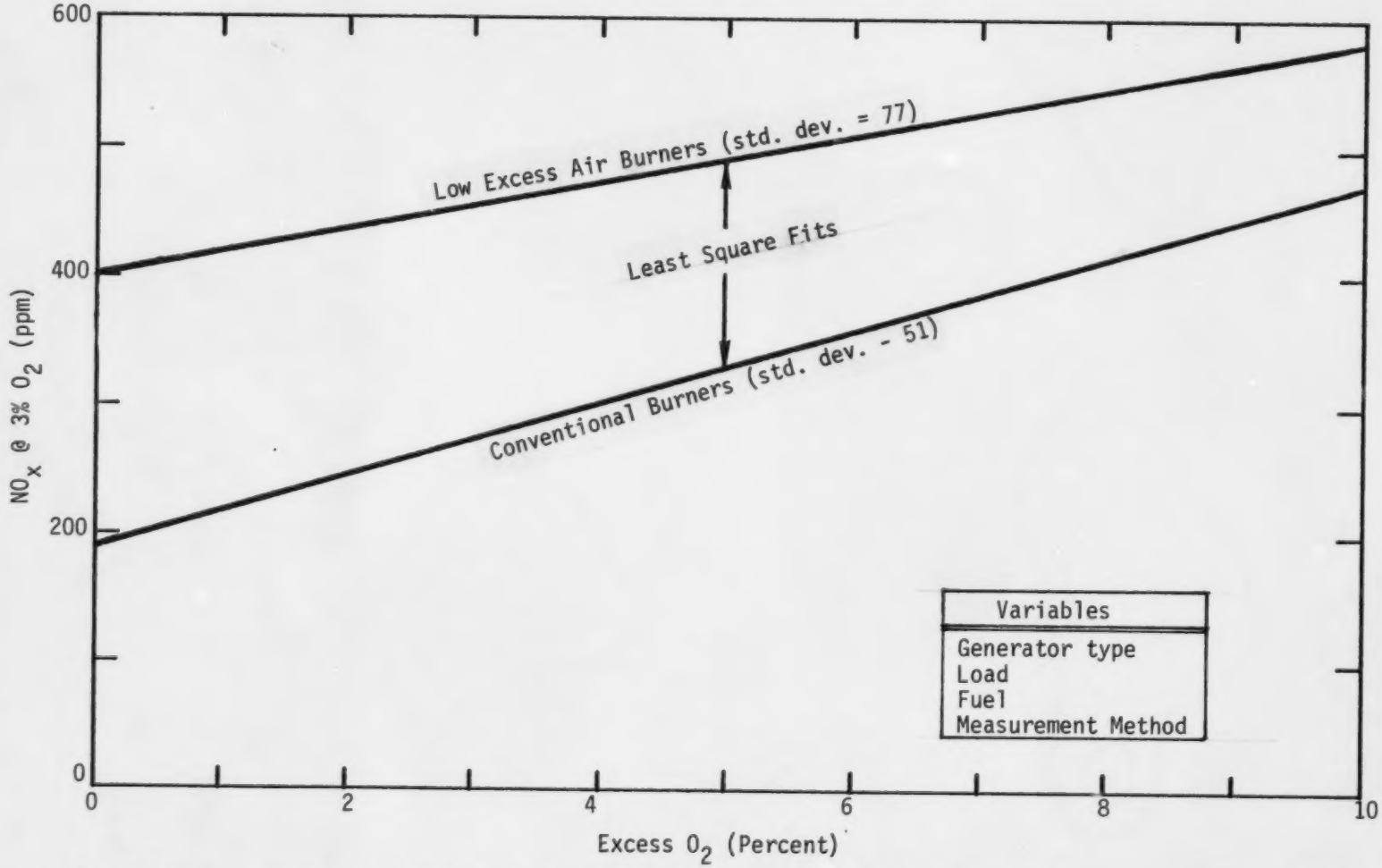


Figure 2-25. Comparison of NO_x emissions from low excess air and conventional burners firing high nitrogen crude oil (50 x 10^6 Btu/hr) (2.11).

2.11

selection of burners (and claims for minimum emissions) is currently available from Japanese firms due to enactment of strict NO_x emissions regulations in Japan in 1975 and 1977. Performance of these burners on high-nitrogen oils is not well documented, however.

A recent study[2.10] investigated NO_x emissions produced by several different commercial and experimental heavy oil burner designs and the level of reduction possible through simple burner modification (i.e., changes in register setting, atomizer spray angle, etc.). The burners investigated are shown in Figure 2-26 and represent burners typically found in watertube and firetube boilers and in a range of process furnaces. In addition, burner staging was also investigated by injecting air through four ports located in the front wall of the test furnace around the burner exit.

Figure 2-27 presents selected results for a comparison of emissions levels from these tests. The different points represent optimized conditions where, for individual burners, the NO_x emission has been minimized and burner parameters trimmed to reduce or control smoke emission levels. The figures also include values for staged and non-staged combustion (using tertiary air ports), and values taken from other burner trials (some with specially developed low NO_x burners) under similar firing conditions. Figure 2-27 shows that there is a strong correlation between NO_x and smoke emissions, and that in the limit this is virtually independent of burner design. If a smoke number in the range of 3 to 4 is considered to be the maximum acceptable, then Figure 2-27 would indicate (for the range of conditions tested) a minimum achievable NO_x emission of between 150 and 200 ppm. It was possible to produce flames with lower NO_x levels, but such flames were usually associated with high smoke emission and/or instability.

In general, it can be concluded that the minimum level of NO_x which is likely to be achieved through combinations of burner modification, burner design, and tertiary air ports alone will be near 150 ppm (at 0 percent O_2). Combinations of low excess air firing, flue gas recirculation, and burner design may further reduce emissions below this level. Very low levels of NO_x

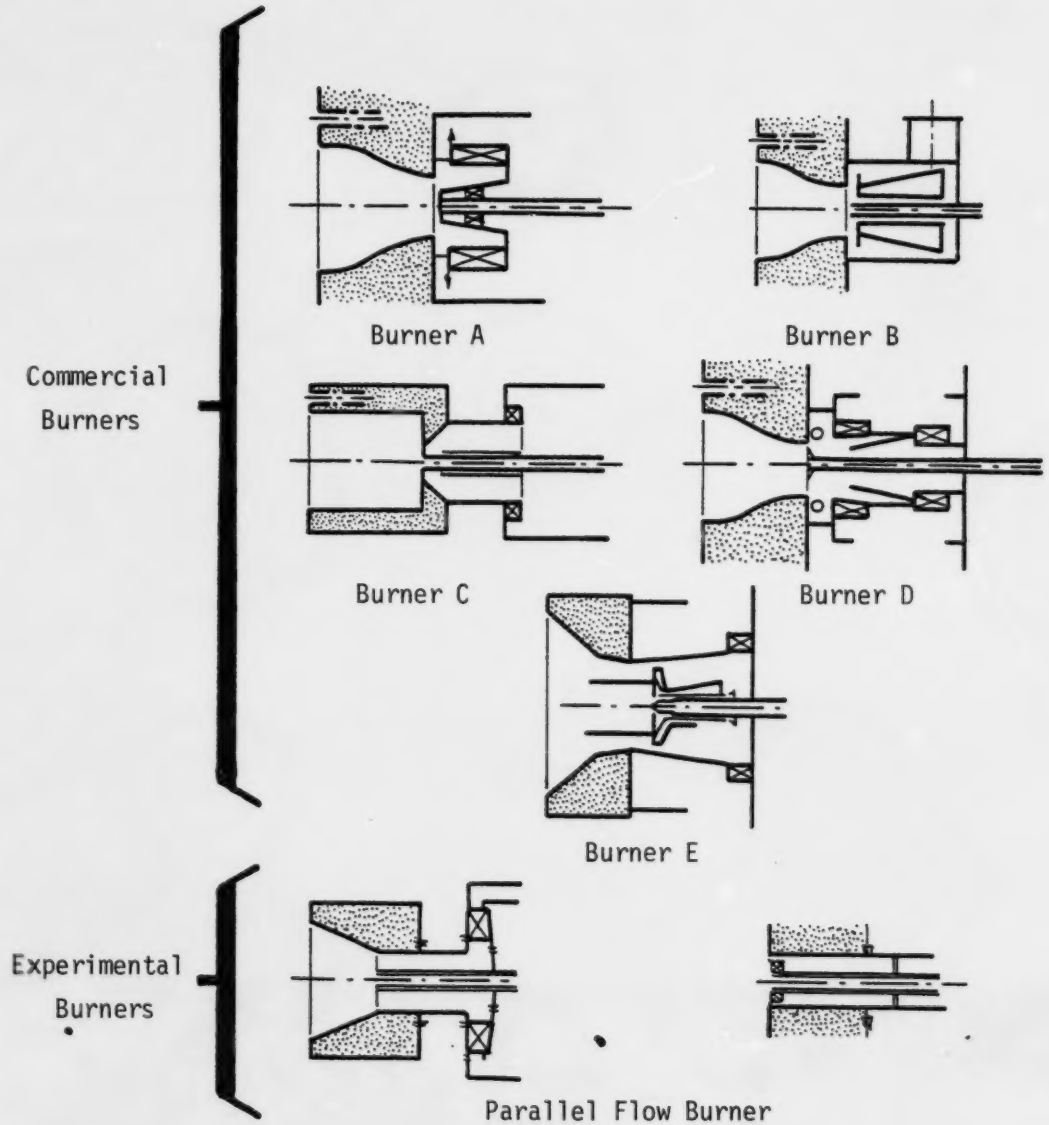


Figure 2-26. Burners tested in burner comparison study [2.10].

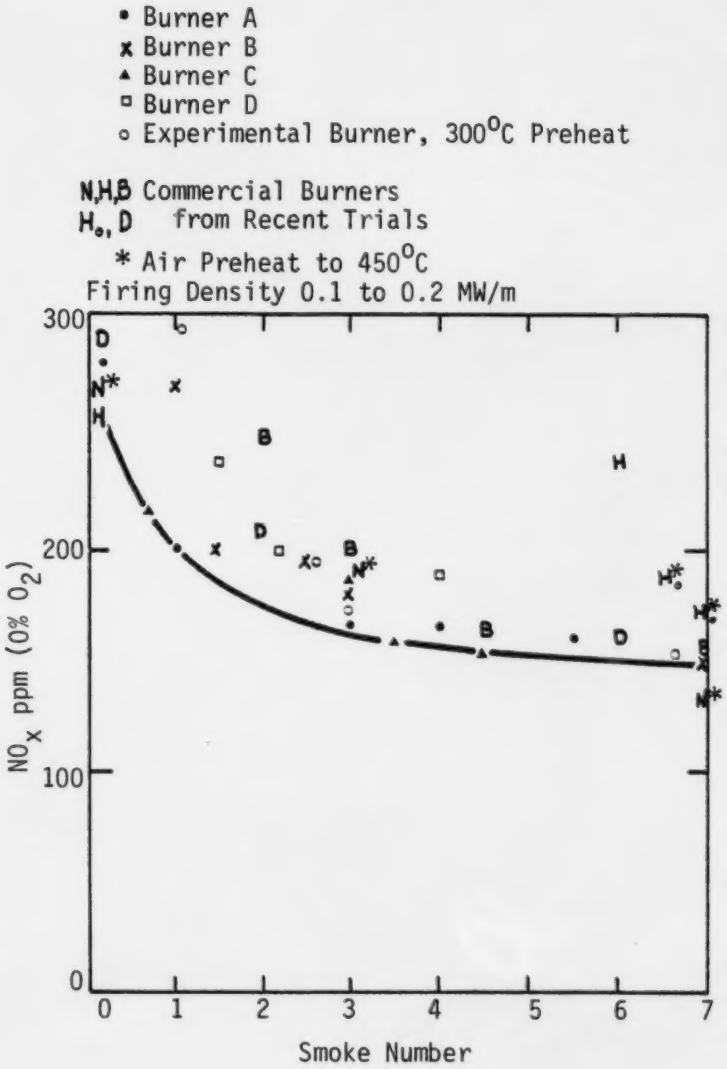


Figure 2-27. Optimized NO_x and smoke emissions from several burners (residual oil). (2.10)

(i.e., below 100 ppm) may only be achievable on high nitrogen oils with advanced two-stage burner designs.

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3.0 BENCH-SCALE RESULTS

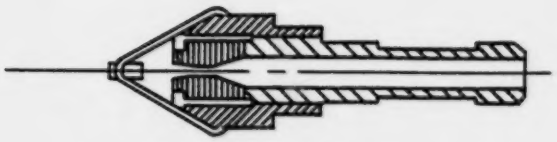
3.1 Purpose and Scope

This portion of the report summarizes the small-scale studies which were conducted initially to define the relationship between fuel chemistry and exhaust emissions under both excess air and staged combustion conditions. The optimization of staged combustor parameters in the fuel-rich primary zone was also studied to provide direct guidance for advanced low NO_x burner design. Under EPA Contract 68-02-2624, 19 liquid fuels were investigated, including 16 petroleum-derived oils (3 distillate and 13 residual fuel oils) and 3 alternate liquid fuels. Fuel blends and/or doped fuels were also investigated. The range of fuels investigated was expanded under this program to include a heavy petroleum crude oil and 6 additional alternative liquid fuels (synfuels). The results of these early fuel screening studies was used as a guide for selecting those fuels tested in the staging optimization studies. In addition to exhaust concentrations, in-flame measurements were made to quantify the influence of first-stage temperature and stoichiometry on the fate of fuel nitrogen species.

3.2 Experimental Systems

3.2.1 Tunnel Furnace

The down-fired tunnel furnace illustrated in Figure 3-1 was designed to allow utilization of commercially available spray nozzles, and yet be capable of testing with artificial atmospheres. This combustor was 21 cm inside diameter. The walls consisted of insulating and high-temperature castable refractories and the full-load firing rate was 0.53 cc/sec, which corresponds to a nominal heat release of 21 kW. All airstreams were metered with precision rotameters. The main combustion air was not preheated. In certain tests the "air" was enriched or replaced with varying amounts of carbon dioxide, argon, and oxygen, all of which were supplied from high-pressure cylinders.



Ultrasonic Twin-fluid Atomizer

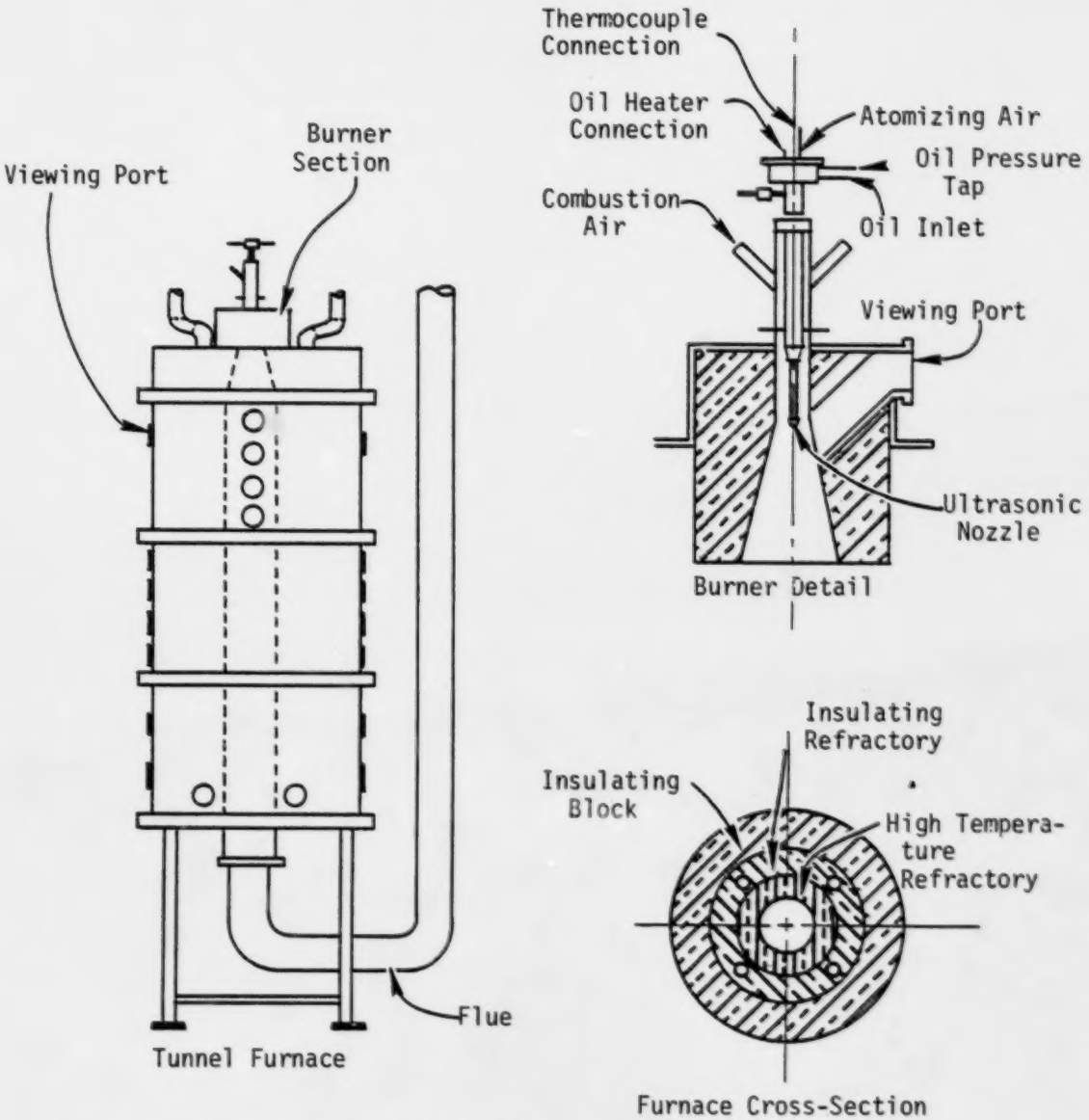


Figure 3-1. Details of the tunnel furnace system.

Fuel and air entered the combustion chamber through the burner illustrated in Figure 3-1. The combustion air was introduced axially (without swirl) and a long refractory burner exit was used (L/D - 5.0). The interchangeable fuel injection system consisted of a 19 mm diameter stainless steel tube which contained the atomizing air supply tube, the fuel oil supply tube, a heater for final oil temperature control, and a chromel/alumel thermocouple positioned in the injector tip, prior to the nozzle for accurate oil temperature measurement. A commercial air-assisted ultrasonic oil atomizer (capacity 0.55 cc/sec) was used in this investigation because it provided adequate atomization of the heavy liquid fuels at relatively low flow rates. The dropsize distribution was narrow and centered at 20 microns[3.1]. The top of the fuel nozzle was positioned at the beginning of the burner divergent section (as shown in Figure 3-1) and, in general, the visible flame front was displaced one to four nozzle diameters from the nozzle tip.

The staged combustion tests were conducted in a separate but similar tunnel furnace illustrated in Figure 3-2. In this system the vertical combustion chamber was 2.3 m long and 15.2 cm in inside diameter. The walls contained slots which allowed insertion of stainless steel cooling coils; thus, the temperature profile within the furnace could be significantly changed by varying the location and number of these coils. The slots were also used for inserting a refractory choke/secondary air injection system. A 5 cm inside diameter choke was used to prevent recirculation of second stage air into the first stage. The secondary air injector was a 10.2 cm diameter stainless steel ring with 24 6.3 mm diameter holes drilled parallel to the axis of the furnace. The injector was designed to provide gradual mixing of the secondary air with the primary combustion products. The velocity ratio of the secondary air to the incoming combustion products was approximately 2 to 1 at a first stage stoichiometry of 0.8. In some tests a second refractory choke was also inserted near the top of the furnace to shield the initial fuel vaporization zone from cooling coils in the first stage. This "radiation choke" made it possible to vary temperatures in the fuel rich hold-up zone without influencing the rate of droplet vaporization and initial combustion.

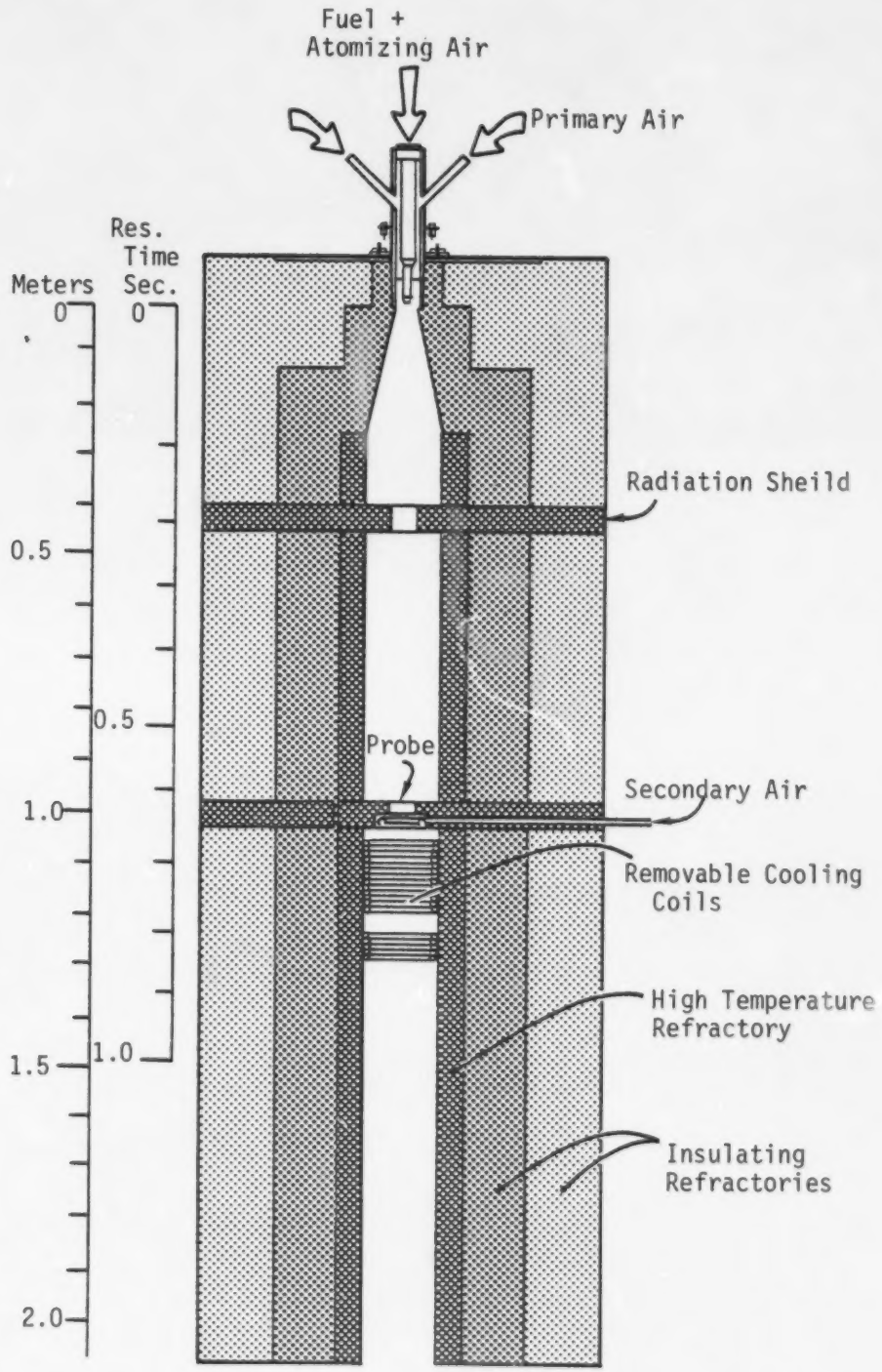


Figure 3-2. Modified tunnel furnace.

3.2.2 Analytical System

Exhaust concentrations were monitored continuously using a chemiluminescent analyzer for NO and NO_x, a NDIR analyzer for CO and CO_2, and a paramagnetic analyzer for O_2. The flue gas was withdrawn from the stack through a water-cooled, stainless steel probe using a stainless steel/Teflon sampling pump. Sample conditioning prior to the instrumentation consisted of an ice bath water condenser and glass-wool and Teflon fiber filters. All sample lines were 6.3 mm Teflon and all fittings were 316 stainless steel.

In-flame temperature measurements were made with a standard suction pyrometer containing a platinum/rhodium thermocouple. In-flame gas samples were withdrawn with a long, stainless steel water-quenched probe. HCN and NH_3 were absorbed in a series of wet impingers and concentrations were determined using specific ion electrodes. The sampling equipment and probe are shown in Figures 3-3 and 3-4. Sulfide ion interference was minimized by the addition of lead carbonate[3.2]. Hydrocarbons were measured using a water-cooled probe, heated sample line, and a FID analyzer.

3.2.3 Fuels

In addition to the fuels previously tested under Contract 68-02-2624, one crude oil and six additional alternative liquid fuels were tested:

- Kern River, California crude oil
- SRC II
- SRC II blend with donor solvent
- SRC II heavy distillate
- Residual shale oil
- 520-850 F shale fraction
- >850 F shale fraction

Analyses of all the fuels tested are given in Table 3-1. The symbols shown in the Table are used through this report wherever fuel comparisons are illustrated.

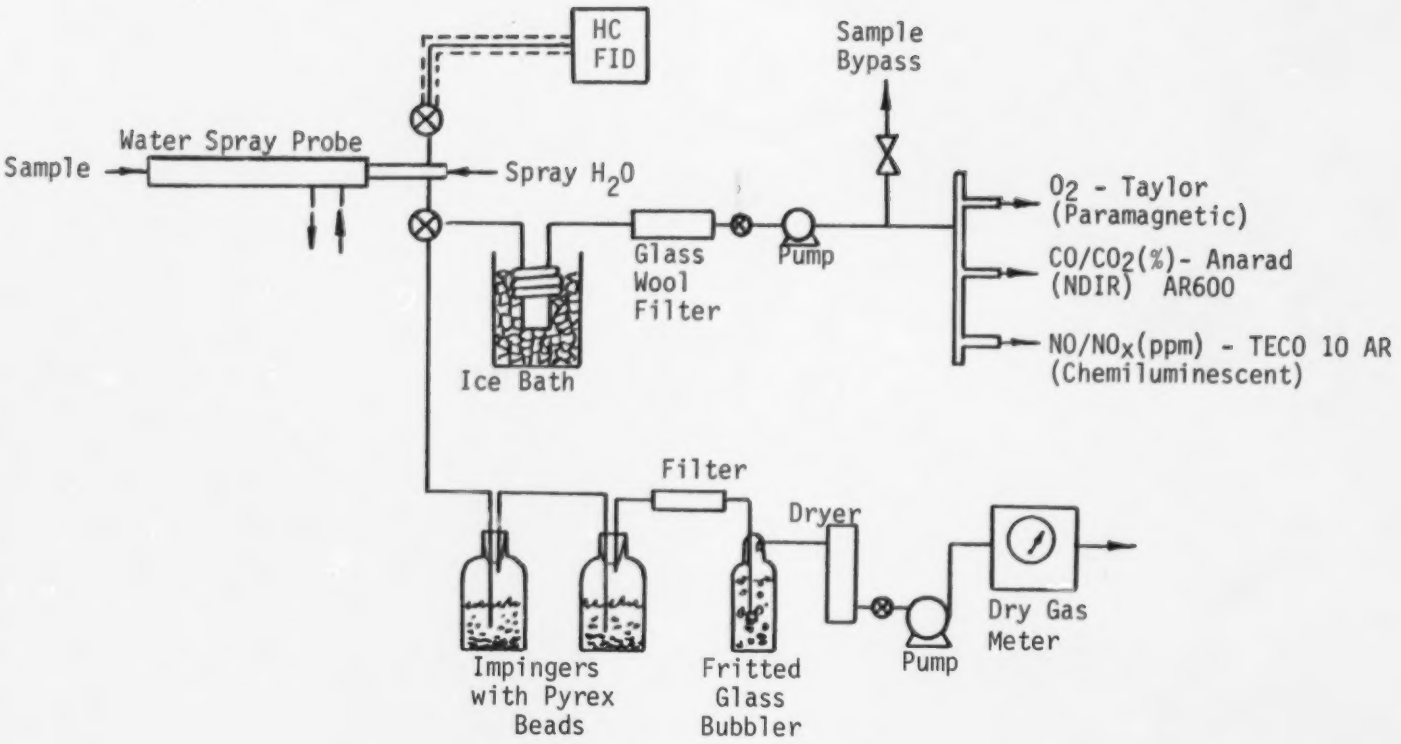


Figure 3-3. Sample train for reduced species measurements.

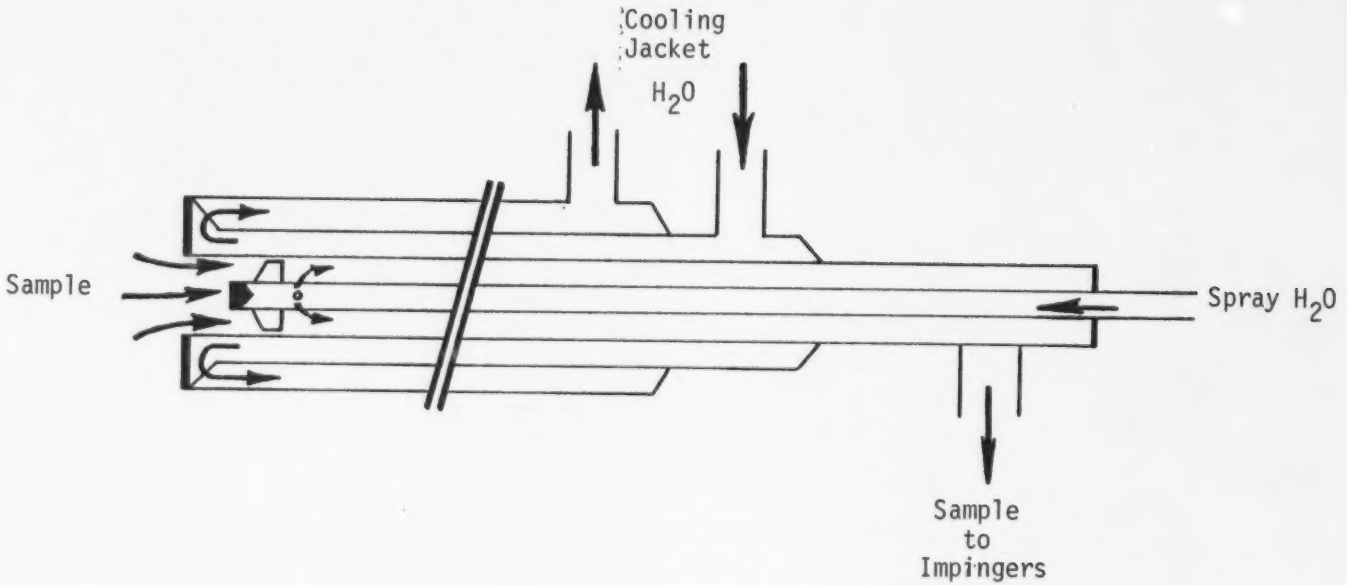


Figure 3-4. Water spray probe used for determining reduced nitrogen species concentrations.

TABLE 3-1. DETAILED FUEL ANALYSES

	D1	D2	D3	R1	R2	R3	R4	R5	R6
Symbol	Alaskan Diesel	W. Texas Diesel	California No. 2 Oil	East Coast	Middle East	Low Sulfur No. 6 Oil	Indo/ Malaysian	Venezuelan Desulfurized	Pennsyl. (Amarada Hess)
Ultimate Analysis:									
Carbon (%)	86.99	88.09	86.8	86.54	86.78	86.57	86.53	85.92	84.82
Hydrogen (%)	12.07	9.76	12.52	12.31	11.95	12.52	11.93	12.05	11.21
Nitrogen (%)	0.008	0.026	0.053	0.16	0.18	0.22	0.24	0.24	0.34
Sulfur (%)	0.31	1.88	0.27	0.36	0.67	0.21	0.22	0.93	2.26
Ash (%)	<0.001	<0.001	<0.001	0.023	0.012	0.02	0.036	0.033	0.067
Oxygen (%)	0.62	0.24	0.36	0.61	0.41	0.46	1.04	0.83	1.3
Conradson Carbon Residue (%)				2.1	6.0	4.4	3.98	5.1	12.4
Asphaltene (%) *				0.34	3.24	0.94	0.74	2.59	4.04
Flash Point, ^{o}F				205	350	325	210	176	275
Pour Point, ^{o}F				50	48	105	61	48	66
API Gravity at 60^{o}F	33.1	18.3	32.6	24.9	19.8	25.1	21.8	23.3	15.4
Viscosity, SSU, at 140^{o}F	33.0	32.0	30.8	131.2	490	222.4	199	113.2	1049
at 210^{o}F	29.5	28.8	29.5	45	131.8	69.6	65	50.5	240
Heat of Combustion:									
Gross Btu/lb			19,330	19,260	19,070	19,110	19,070	18,400	18,520
Net Btu/lb				18,140	17,980	17,970	17,980	17,300	17,500
Calcium, ppm				7.1	1.2	9.52	14	8.7	9.2
Iron, ppm				16	2.6	123.6	16	6.5	13.2
Maganese, ppm				0.09	0.02	0.46	0.13	0.09	0.10
Magnesium, ppm				3.7	0.08	2.23	3.6	3.6	3.3
Nickel, ppm				6.7	13	14.10	19		32.7
Sodium, ppm				37	0.98	3.74	15		64.5
Vanadium, ppm				14	25	3.11	101		81.5

* ASTM D-189

TABLE 3-1. DETAILED FUEL ANALYSES (CONT.)

	R7	R8	R9	R10	R11	R12	R13	R14
Symbol	Gulf Coast ◇	Venezuelan ⌂	Alaskan □	Calfornia ▽	California ○	California ◊	California ✕	Kern River Crude Oil ◊
Ultimate Analysis:								
Carbon (%)	84.62	85.24	86.04	85.75	85.4	85.33	86.66	86.61
Hydrogen (%)	10.77	10.96	11.18	11.83	11.44	11.23	10.44	10.93
Nitrogen (%)	0.36	0.40	0.51	0.62	0.77	0.79	0.86	0.83
Sulfur (%)	2.44	2.22	1.63	1.05	1.63	1.60	0.99	1.16
Ash (%)	0.027	0.081	0.034	0.038	0.043	0.032	0.20	0.030
Oxygen (%)	1.78	1.10	0.61	0.71	0.71	1.02	0.85	0.44
Conradson Carbon Residue (%)	14.8	6.8	12.9		8.74	9.22	15.2	8.3
Asphaltene (%) *	7.02	8.4	5.6		5.18	5.18	8.62	3.92
Flash Point, ^{o}F	155	210	215			150	180	255
Pour Point, ^{o}F	40	58	38		38	30	42	65
API Gravity at 60^{o}F	13.2	14.1	15.6	19.5	15.4	15.1	12.6	12.3
Viscosity, SSU, at 140^{o}F	835	742	1,071	246.1	854	748	720	4,630
at 210^{o}F	181	196.7	194	70	129	131.6	200	352
Heat of Combustion:								
Gross Btu/lb	18,240	18,240	18,470		18,470	18,460	18,230	18,430
Net Btu/lb	17,260	17,400	17,580		17,430	17,440	17,280	17,430
Calcium, ppm	4.4	9.1	6.9		21	14	90.6	4.4
Iron, ppm	19	11	24		73	53	77.2	15
Manganese, ppm	0.13	0.09	0.06		0.8	0.1	0.87	0.15
Magnesium, ppm	0.4	3.8	1.4		5.1	3.8	31.4	1.1
Nickel, ppm	29	52	50		65	82	88	68
Sodium, ppm	3.6	32	37		21	2.6	22.3	3.4
Vanadium, ppm	45	226	67		44	53	66.2	39

* ASTM D-189

TABLE 3-1. DETAILED FUEL ANALYSES (CONT.)

	A1	A2	A3	A4	A5	A6	A7	A8	A9
Symbol	Shale-Derived DFM	Synthoil	Crude Shale (Paraho)	SRC/Donor Solvent Blend	Residual Shale	SRC II	Shale Fraction (520-850°F)	Shale Fraction (+850°F)	SRC II Heavy Distillate
Ultimate Analysis:									
Carbon (%)	86.18	86.30	84.6	89.91	86.71	85.91	86.39	85.92	88.98
Hydrogen (%)	13.00	7.44	11.3	9.27	12.76	8.74	11.53	10.61	7.64
Nitrogen (%)	0.24	1.39	2.08	0.45	0.46	0.96	1.92	2.49	1.03
Sulfur (%)	0.51	0.80	0.63	0.065	0.28	0.30	0.72	0.63	0.39
Ash (%)	0.003	1.56	0.026	0.004	0.009	0.04	0.002	0.24	0.058
Oxygen (%)	1.07	2.54	1.36	0.30	0.03	4.08	0.44	0.11	1.90
Conradson Carbon Residue (%)	4.1	23.9	2.9	6.18	0.19	0.51	0.07	9.3	
Asphaltene (%)	0.036	16.55	1.33	4.10	0.083		0.12	4.24	
Flash Point, °F	182	210	250	70	235	173	255	370	265
Pour Point, °F	40	80	80	72	90	-55	70	95	8
API Gravity at 60°F	33.1	S=1.14	20.3	10.0	29.0		22.3	12.0	1.3
Viscosity, SSU, at 140°F	36.1	10,880	97	40.6	54.3	39	62.9	3050	67.2
at 210°F	30.7	575	44.1	32.5	37.3		41.8	490	41.3
Heat of Combustion:									
Gross Btu/lb	19,430	16,480	18,290	17,980	19,350	17,100	18,529	18,000	17,120
Net Btu/lb	18,240	15,800	17,260	17,130	18,190		17,470	17,030	16,240
Calcium, ppm	0.13	1,670	1.5	0.33	4.20		<0.05	238	
Iron, ppm	6.3	109	47.9	3.9	<0.5		2.9	86	
Manganese, ppm	0.06	6.2	0.17	<0.5	<0.5		0.033	1.3	
Magnesium, ppm		170	5.40	0.17	0.15		0.021	51	
Nickel, ppm	0.43	2.6	5.00	<0.5	<0.5		<0.5	7.4	
Sodium, ppm	0.09	148	11.71	0.31	2.51		<0.1	11	
Vanadium, ppm	<0.1	6.5	<0.3	<1.0	<1.0		<0.2	1.1	

* ASTM D-189

Previous work has shown that total fuel nitrogen content is the only first-order parameter controlling nitrogen oxide emissions under normal combustion conditions[3.3]. Fuel nitrogen content ranged from less than 0.01 percent to 0.05 percent for the petroleum distillate fuels, from 0.16 to 0.86 percent for the residual and crude petroleum oils, and from 0.24 to 2.49 percent for the synfuels. Figure 3-5 illustrates the wide spectrum of fuel composition investigated. In Figure 3-5a, nitrogen content of the fuels is shown as a function of sulfur content. Sulfur content ranged from 0.2 to 2.22 percent for the petroleum-derived fuels and was less than 0.8 percent for all the petroleum fuels. Carbon-to-hydrogen has been linked with the propensity of a certain fuel to form soot[3.4]. As seen in Figure 3-5b, C/H ratio for the synfuels is higher than most of the petroleum fuels, except for the shale DFM and residual shale oils which had been extensively hydrotreated.

Conradson carbon residue is generally used as an indication of the coking tendency of heavy fuel oils, and coking is generally associated with increased particulate emissions. Figure 3-5c shows that Conradson carbon residue of the synthetic liquids was generally lower than most of the heavy residual oils, with the exception of the very heavy synfuels--Synthoil and the >850°F shale fraction. These figures suggest that the nature of particulate emissions from synfuels will be quite different from conventional residual fuels, potentially containing a much higher percentage of fine (and therefore respirable) soot-like particulate.

The rate at which the fuel droplets vaporize and the volatility of the fuel nitrogen compounds can effect the degree of NO_x control achievable in a staged combustion system[3.3]. Figure 3-6 shows the results of vacuum distillates data taken by an independent testing laboratory. In general, the synfuels were lighter fuels than their petroleum counterparts, with 50 percent mass evolved averaging approximately 700°F as compared to approximately 850°F for the residual petroleum oils. The synfuels also produced lower residuum yields, with typically 80 to 99 percent of mass evolving as vapor compared to only 40 to 70 percent for the residual petroleum oils. Two synfuels--residual shale and >850°F shale fraction--were

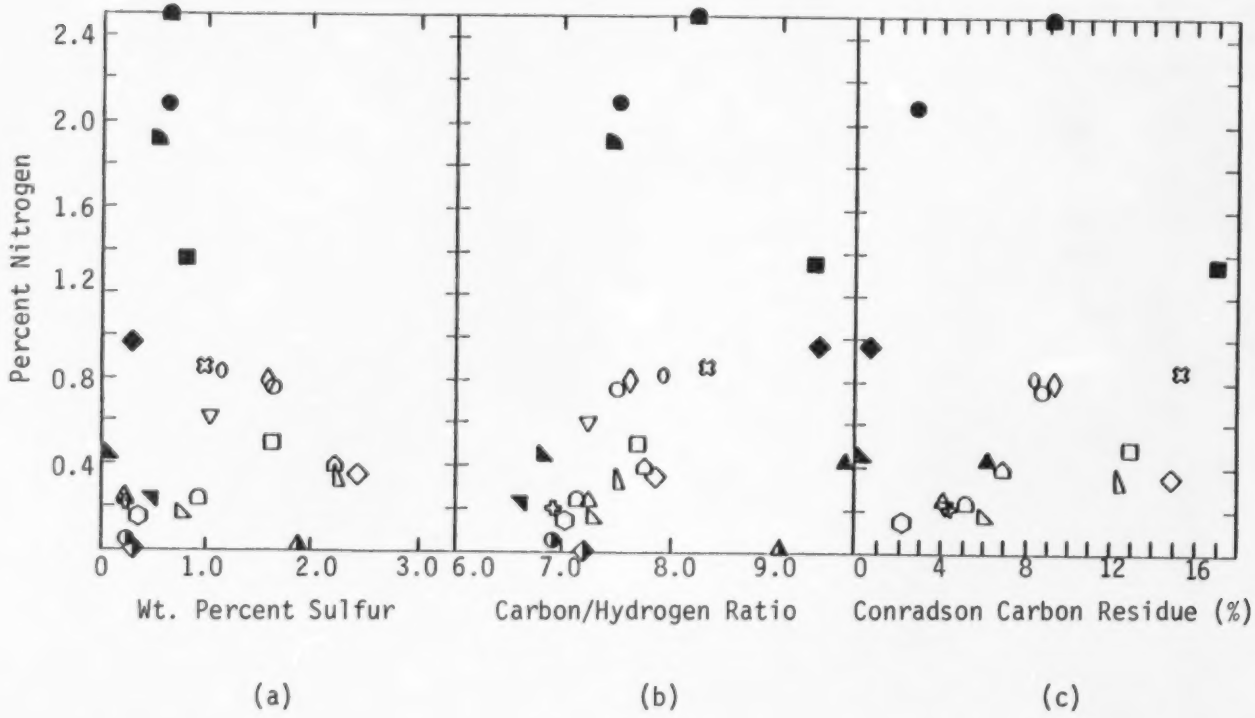


Figure 3-5. Properties of fuels tested (refer to Table 3-1 for key to symbols).

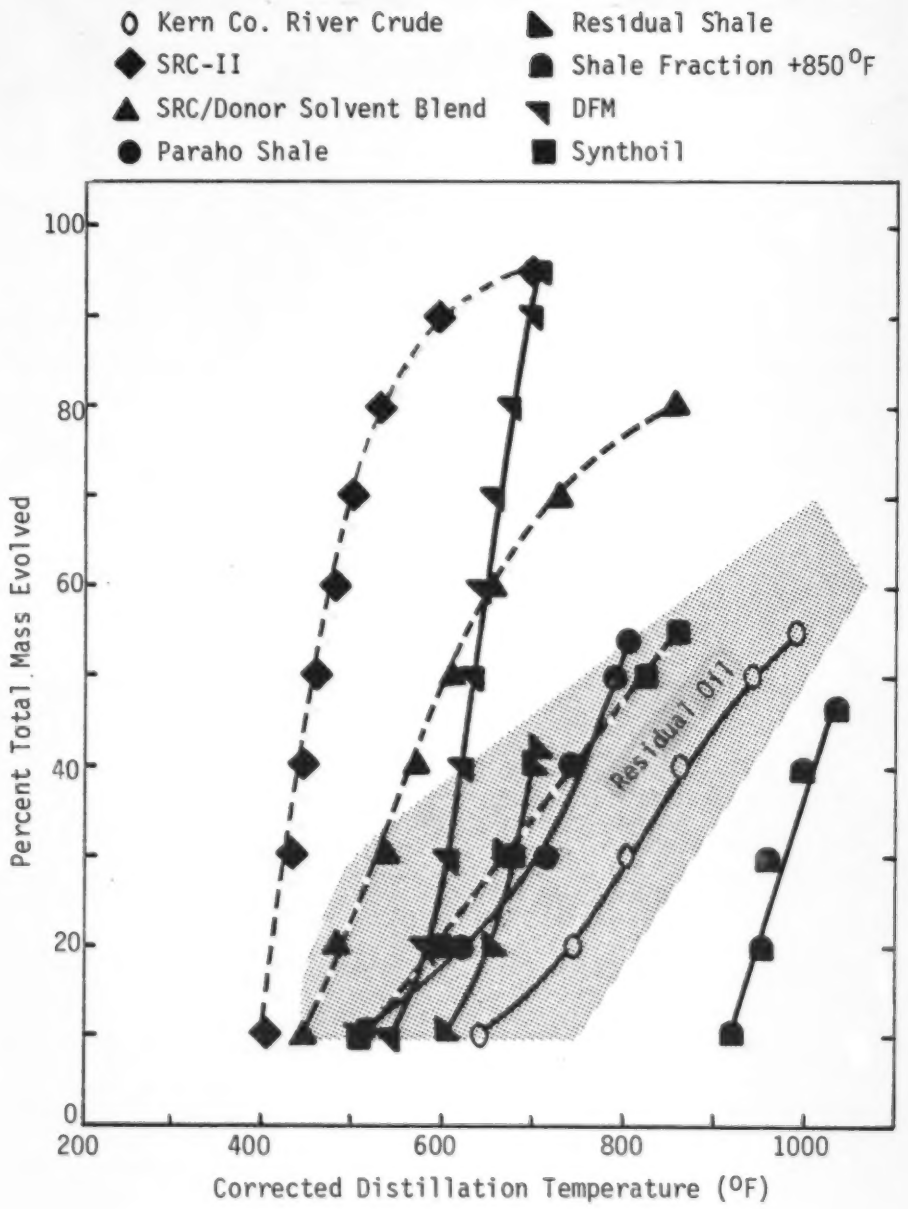


Figure 3-6. Vacuum distillation data - mass evolution.

comparatively low volatility fuels. The distillation fractions of several oils were analyzed for nitrogen content, thus giving an indication of the fuel nitrogen volatility. Figure 3-7 shows nitrogen evolved as a function of distillation temperature. Nitrogen from the synfuels evolved considerably earlier than the residual petroleum oils and must greater nitrogen yields were obtained. Based on the results of the previous study, this suggests that although the synfuels contain greater quantities of fuel nitrogen than conventional fuels, and therefore have potential for much higher NO_x emissions when burned, NO_x emissions reduction by the application of two-stage combustion may be more effective than for residual petroleum fuels.

The Kern River crude oil is typical of fuels being burned in California oil fields, high both in nitrogen and sulfur content. The distillation data indicate that although the crude oil is very heavy (API gravity of 12), its evolution characteristics are similar to the heavier residual petroleum oils.

It should be remembered that the temperatures at which nitrogen is evolved will probably be different in flames. However, it is considered that the results obtained with vacuum distillations provide a qualitative ranking for the "refractoriness" of the fuel nitrogen.

The reader should consult Reference 3.3 for further information on properties of petroleum residual oils tested in this study.

3.3 Results - Fuel Screening Experiments

The purpose of this series of experiments was to investigate the effect of fuel composition, both chemical and physical, on the formation of total and fuel NO_x. Fuel composition and dropsize effects could be more easily examined in the small tunnel furnace because (1) many of the widely different fuels were only available in small quantities; (2) the combustion variables could be more precisely controlled in the tunnel furnace; and (3) fuel and thermal NO_x could be separated by the use of artificial oxidants. The majority of the fuel screening studies were carried out under a previous program (EPA Contract 68-02-2624). In that study, 19 fuels were investigated

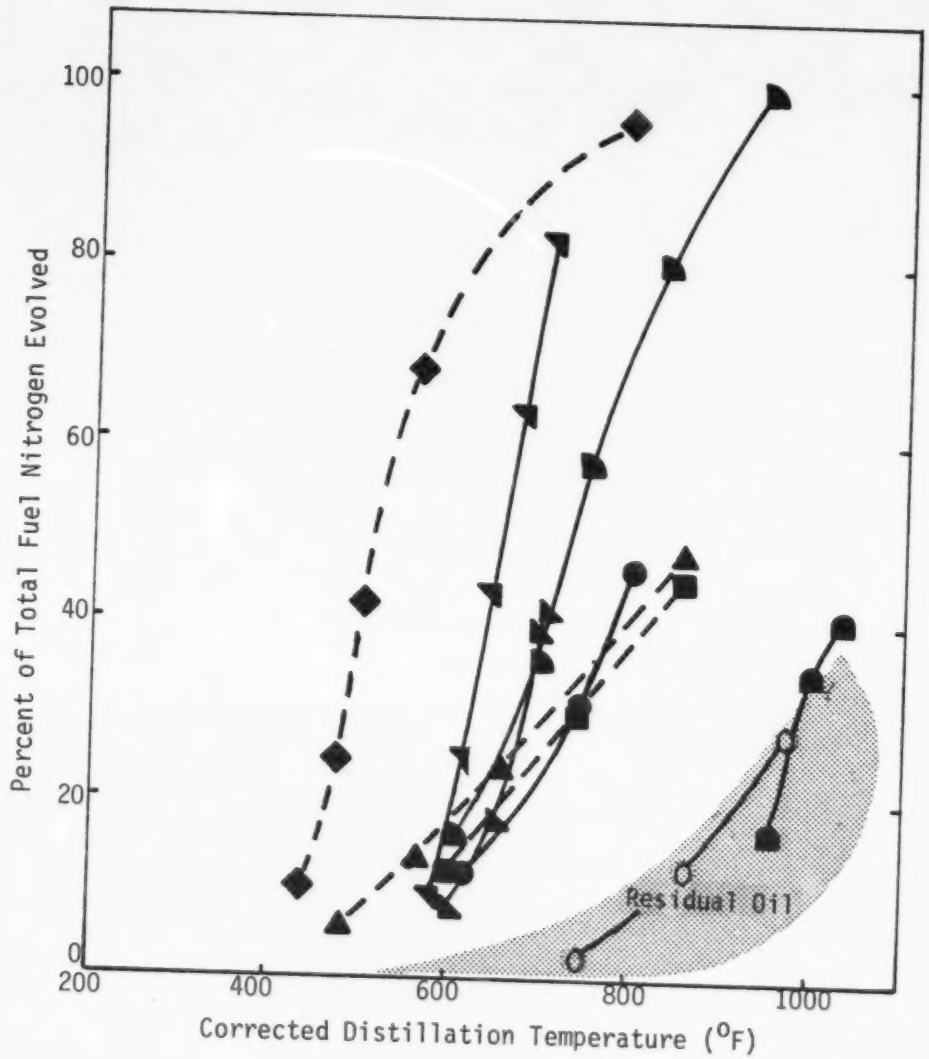


Figure 3-7. Vacuum distillation data - nitrogen evolution.

(16 conventional distillate and residual petroleum-derived fuels and 3 alternative synfuels). In addition to the pure fuels, 14 doped and/or blended fuels were also investigated. The major conclusion from those studies was that under excess air conditions total fuel nitrogen was the only primary fuel parameter controlling the formation of fuel NO_x. The objective of the experiments conducted under the current program was to expand the range of alternative fuels investigated. Among these additional synfuels were coal-derived liquids more typical of those likely to be produced in the future.

Fuel NO_x was isolated under excess air conditions in the tunnel furnace by the replacement of the normal combustion air with a mixture of argon, oxygen, and carbon dioxide, thereby eliminating the formation of NO from molecular nitrogen in the combustion air. Thermal NO_x is defined as the difference between emissions obtained when burning the fuel in air and when burning the fuel in the nitrogen-free oxidant. It is believed that these measurements approximate the NO_x that results from oxidation of the fuel nitrogen during normal combustion. However, the possibility of fuel NO/thermal NO interactions was addressed in the previous study(3.3). In that study, fuel NO_x was determined by two methods:

(1) by the difference in NO_x emissions when burning pure distillate oil oil (containing negligible fuel nitrogen) and nitrogen-containing residual oils in air;

(2) by burning nitrogen-containing fuels in $Ar/O_2/CO_2$.

Fuel NO_x determined by these methods was similar, indicating that fuel NO_x formation was similar in the presence (Method 1) and absence (Method 2) of thermal NO_x formation. These experimental results were also supported by kinetic modeling studies (3.14) which showed that the replacement of N_2 with Ar and CO_2 did not significantly affect NO formation under excess air conditions. In summary, considerable effort was expended in the previous study to investigate the $Ar/O_2/CO_2$ replacement technique for fuel NO_x

definition. It appeared to give a reasonable indication of the amount of fuel nitrogen being oxidized in the flame zone under excess air conditions.

Fuels were screened under both staged and excess air combustion conditions. Fuel NO_x was not determined under staged conditions because of a potential kinetic effect of adding carbon dioxide into the first stage. Smoke emissions were not routinely measured during the small-scale testing, but typically were low due to the hot refractory walls throughout the furnace. All NO_x concentrations are reported in a dry dilution-free (0 percent O_2) basis.

3.3.1 Excess Air Results

Petroleum Crude

Figure 3-8 shows data obtained burning the Kern River crude oil under the standard test conditions (combustion air preheat of 405 K; firing rate of 0.55 cc/sec; ultrasonic nozzle; 205 kPa atomization air pressure). The fuel oil was preheated to approximately 410 K prior to atomization in order to maintain fuel viscosity at approximately 14 $\pm$ 2 cst. The upper curve in Figure 3-6 represents NO_x emissions obtained when burning the fuel in normal air. The lower curve, labeled fuel NO_x, represents emissions obtained when burning the fuel in a 59 percent Ar/21 percent O_2/20 percent CO_2 mixture. Emissions were relatively insensitive to overall excess air. Figure 3-9 is a composite plot of total and fuel NO_x emissions for all of the pure and doped petroleum-derived fuels (at 5 percent excess O_2). Fuel NO emissions from the Kern River crude compared well to fuel NO from the other petroleum fuels. However, thermal NO was slightly higher. This may be due to the presence of light hydrocarbon fragments usually distilled out of residual fuels, which can cause higher flame peak temperatures and higher local combustion intensities.

Alternate Fuels

Six additional alternative liquid synfuels ranging in nitrogen content from 0.45 to 2.49 percent were tested in this program. Figures 3-10 - 3-14

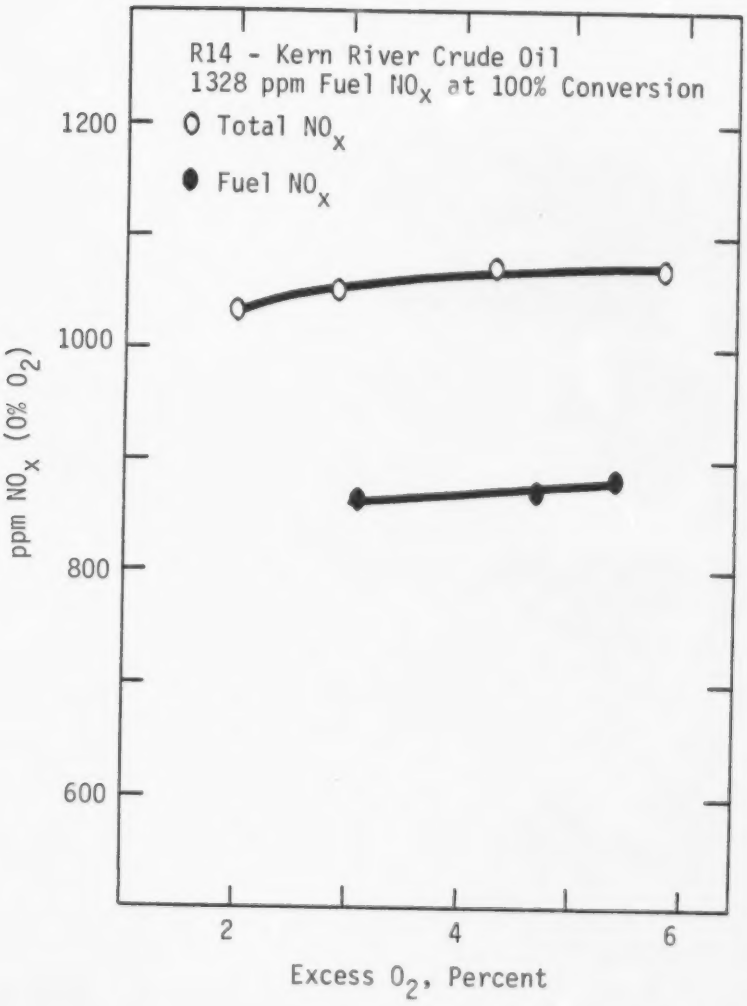


Figure 3-8. Kern County crude oil (R14) - standard test conditions.

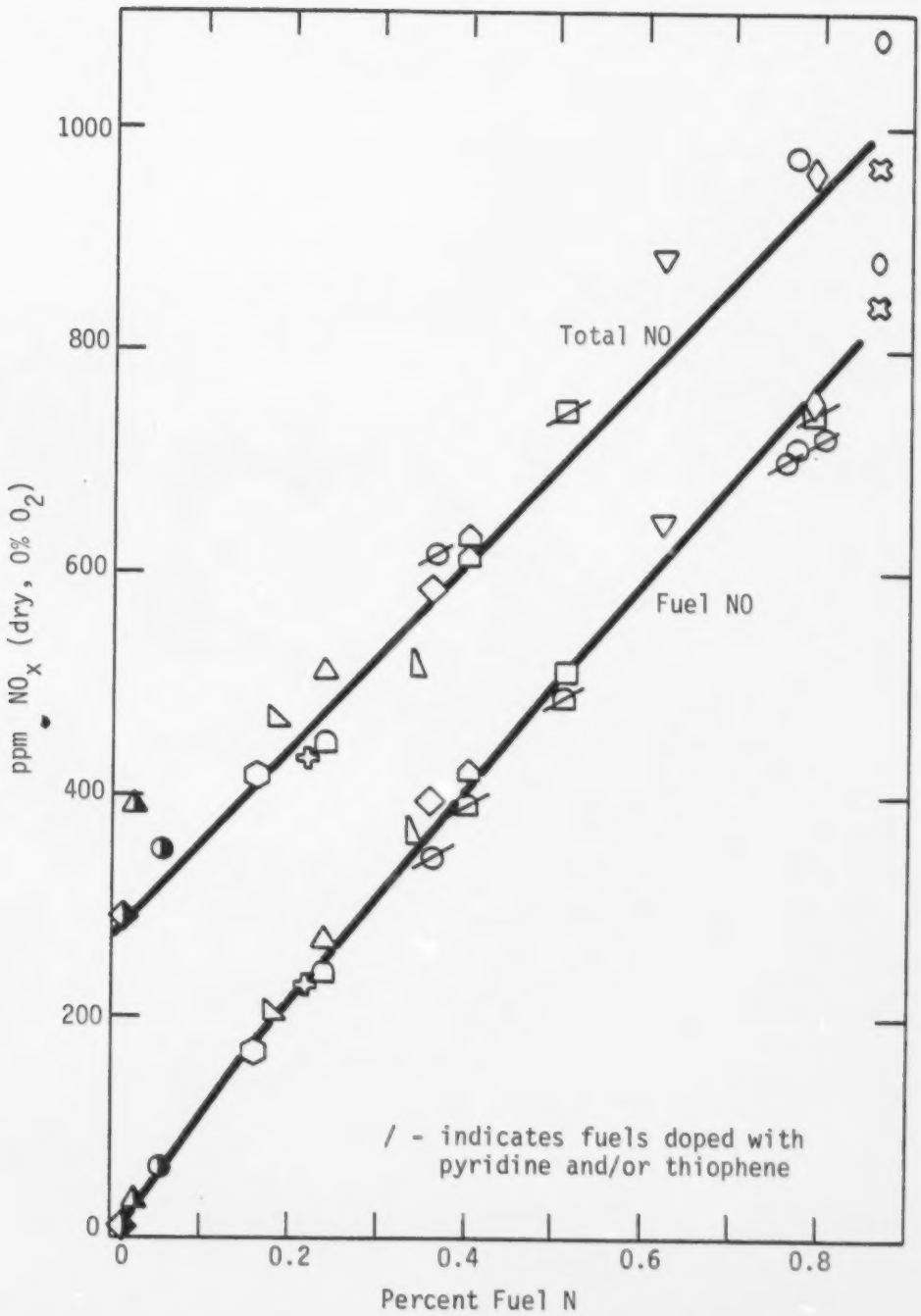


Figure 3-9. Effect of fuel nitrogen on total and fuel NO - pure and doped petroleum fuels.

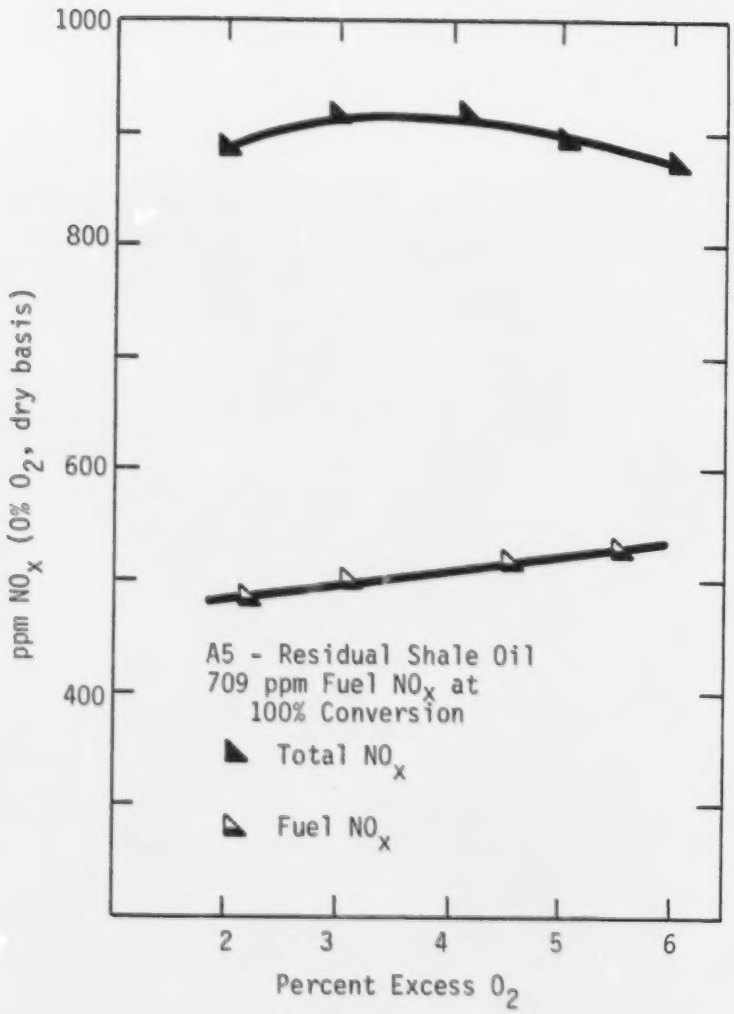


Figure 3-10. Residual shale oil (A5) - standard test conditions.

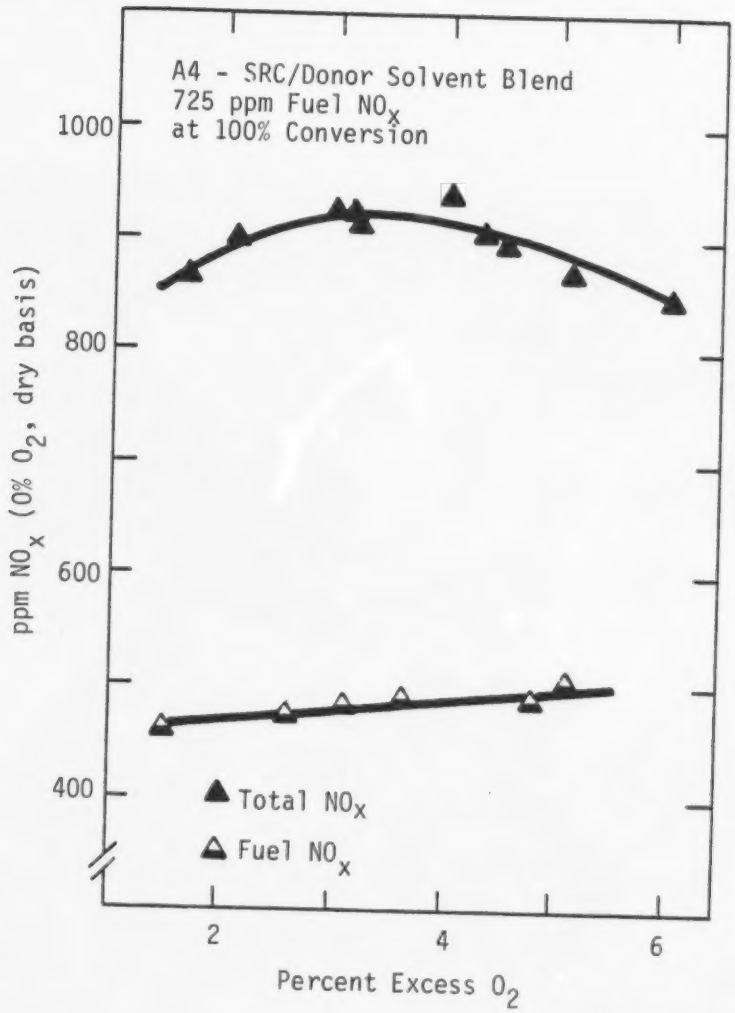


Figure 3-11. SRC/donor solvent blend (A4) - standard test conditions.

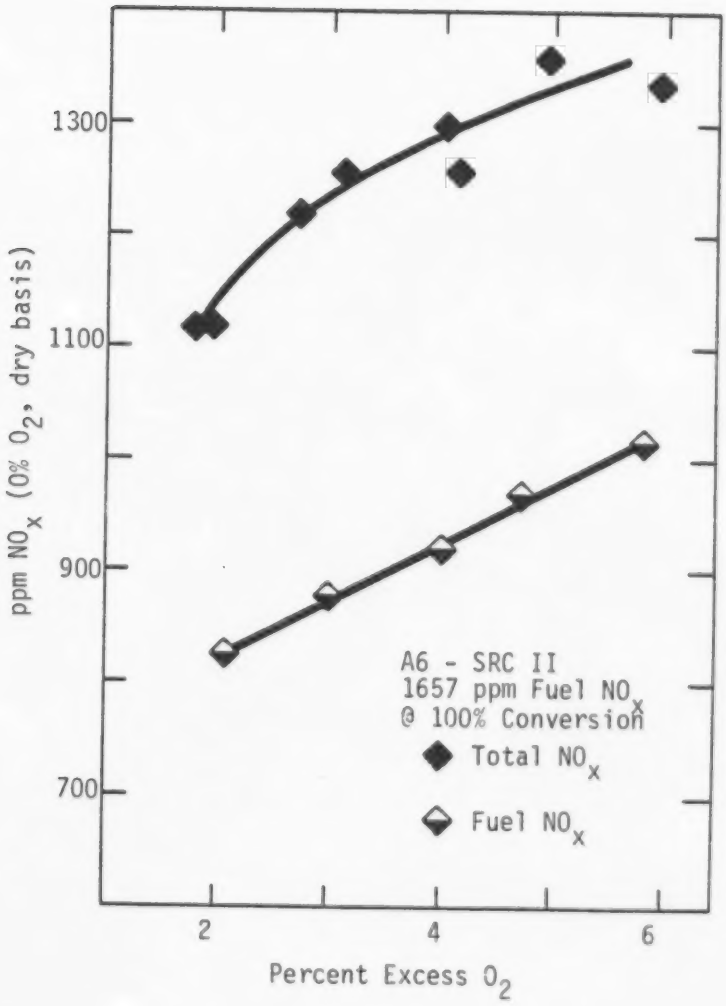


Figure 3-12. SRC II (A6) - standard test conditions.

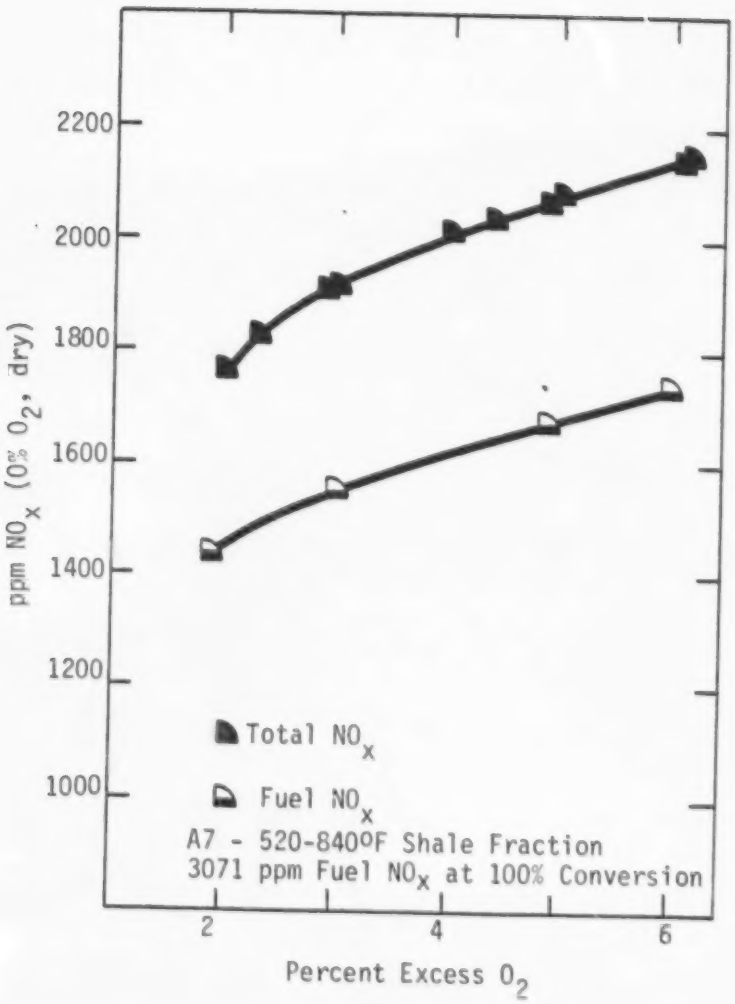


Figure 3-13. 520-840°F shale fraction (A7) - standard test conditions.

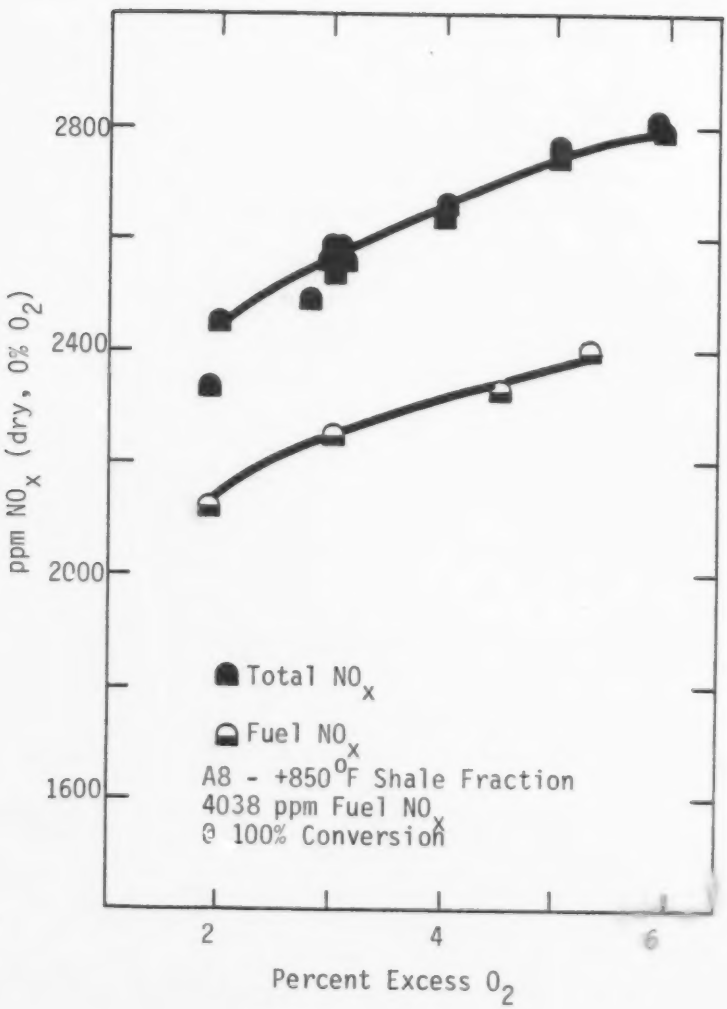


Figure 3-14. +850°F shale fraction (A8) - standard test conditions.

summarize the data taken with these additional alternate fuels. As in the case of the petroleum liquids, the data were obtained in the tunnel furnace with the ultrasonic nozzle, atomization pressure of 205 kPa, combustion air preheat = 405 K, and firing rate = 0.55 cc/sec. In each case both total and fuel NO_x emissions were determined as a function of excess oxygen.

In general, NO_x emissions from the alternate fuels were significantly higher than petroleum oils, reflecting their relatively higher fuel nitrogen content. Total NO_x emissions at 5 percent excess oxygen ranged from 900 ppm (corrected to 0 percent O_2) for the residual shale oil, containing 0.46 percent fuel nitrogen to 2800 ppm for the +800 F shale residuum fraction containing 2.49 percent fuel nitrogen. As with petroleum fuels, NO_x emissions increased with increasing fuel nitrogen.

Figure 3-15 presents these results as a function of fuel nitrogen content for all the fuels tested. In general, fuel NO correlates similarly with fuel nitrogen content for both synthetic and petroleum-derived fuels. Thermal NO (defined as the difference between total and fuel NO_x) from the residual petroleum fuels was relatively constant; however, for several of the alternate fuels higher levels of thermal NO were measured. This may be related to the volatility of the fuels and the fuel nitrogen.

In Figure 3-16 fuel NO_x data are presented as a percentage conversion of the fuel nitrogen to NO_x. In general, the percentage conversion of the fuel nitrogen decreases rapidly to about 0.3 percent nitrogen. Beyond this point, further increases in fuel nitrogen resulted in only a relatively small decrease in the fuel conversion. For a given nitrogen content, conversion for the petroleum-derived and alternate coal- and shale-derived liquids was similar.

In summary, under excess air conditions the conversion of fuel-bound nitrogen in alternative fuels was approximately what could be expected based on the results from petroleum-derived fuels. No significant differences between conventional fuels and synfuels were observed with the exception of slightly higher thermal NO formation in the case of some of the alternative

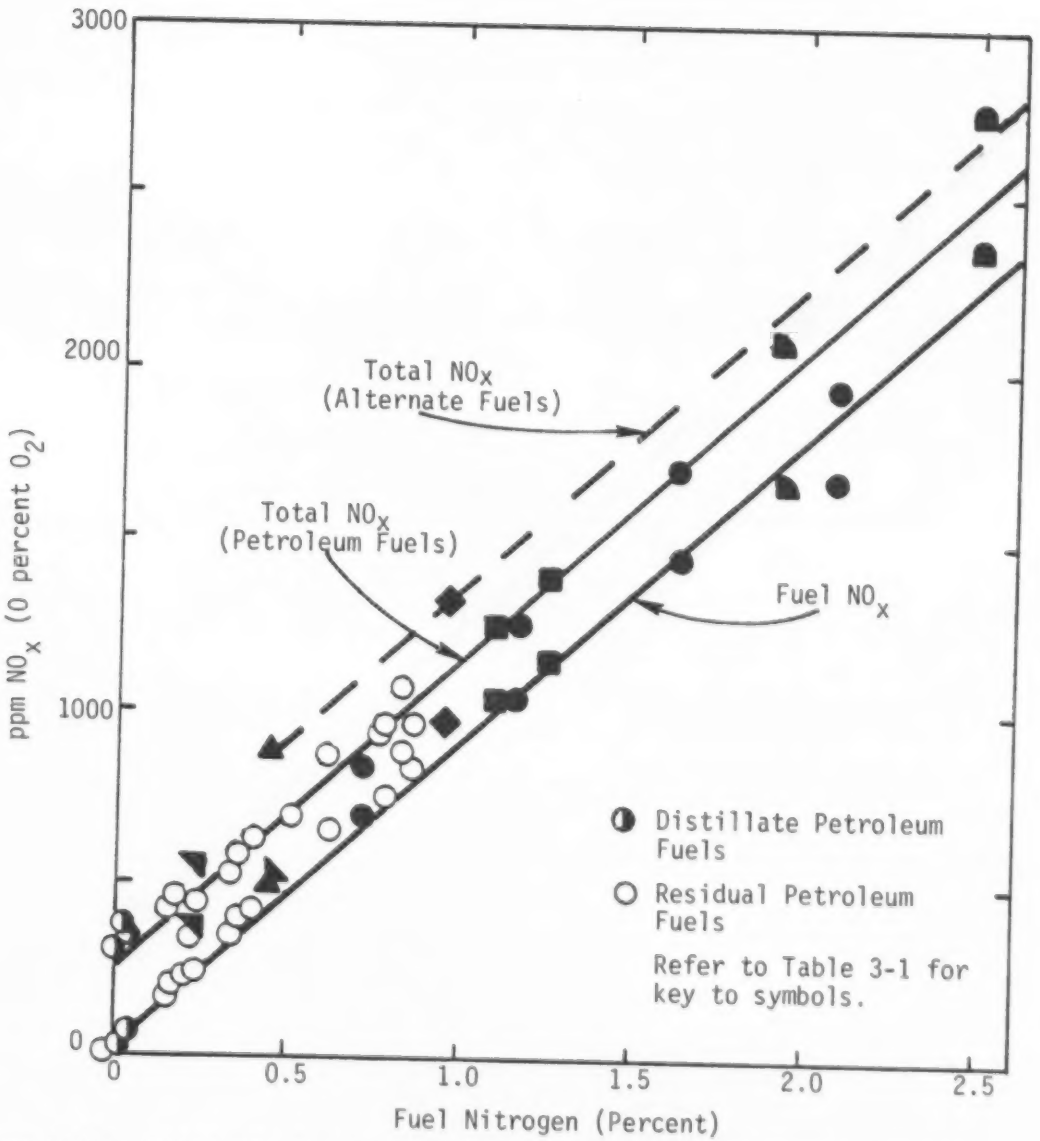


Figure 3-15. Total NO_x (upper curve) and fuel NO_x (lower curve) for all fuels tested versus fuel nitrogen (normal combustion, 5 percent O_2).

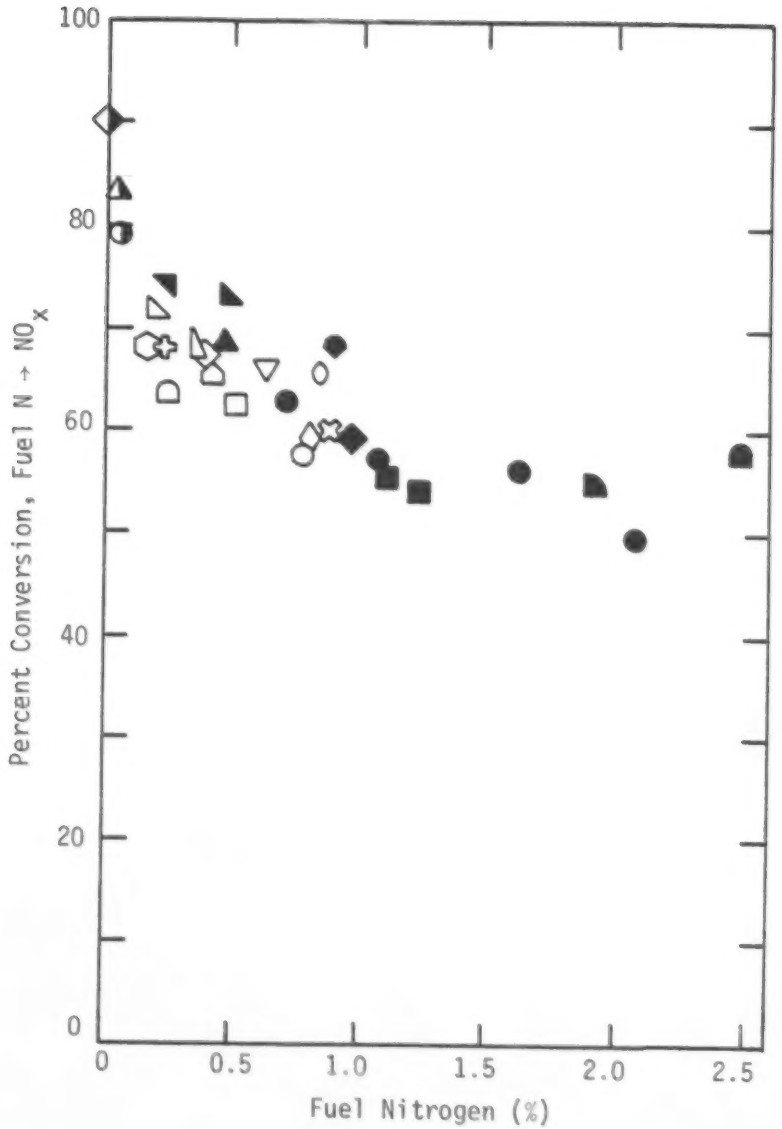


Figure 3-16. Excess air results - comparison of fuel nitrogen conversion for synthetic and conventional liquid fuels (standard test conditions).

fuels. The level of fuel nitrogen conversion obtained in the small scale furnace is higher than is normally expected in practical combustion system (typically 25 to 50 percent) because of the rapid fuel air mixing characteristic of the burner system used in this work; however, the relative ranking of the fuels has been shown to give an indication of trends observed in pilot-scale experiments.

3.3.2 Staged Combustion Results

The additional synthetic fuels received in this contract were screened under staged combustion conditions in order to determine whether the same degree of NO_x reduction could be achieved as with petroleum-derived fuels. Staging was achieved in the tunnel furnace by splitting the combustion air into two streams. The primary air stream was injected with the fuel and the second stage air was injected through two water-cooled air injection lances which could be inserted into the furnace through a series of sample ports along the length of the furnace. The tip of these lances was designed to inject the air at a relatively high velocity (21 - 30 m/sec) normal to the furnace flow, resulting in rapid mixing of the second stage air with the primary zone combustion products. Two secondary air injection locations were investigated, designated Port 2 and Port 4, corresponding to primary zone residence time (calculated at $SR_2 = 0.7$) of 400 msec and 800 msec, respectively. Primary combustion air was preheated to 405 K. Second stage air was not preheated. Overall excess oxygen was held constant at 3 percent. Figures 3-17 through 3-21 summarize the staged combustion results obtained from the five alternative liquid fuels tested.

In Figure 3-17 NO_x emissions are shown as a function of primary zone stoichiometric ratio for the residual shale oil staged at 400 msec (Port 4). Staging was effective in reducing NO_x from approximately 900 ppm under unstaged conditions to approximately 145 ppm at a primary zone stoichiometric ratio of 0.75. NO_x emissions from the coal derived SRC/donor solvent blend (A4 - Figure 3-18), which has approximately the same fuel nitrogen content as the residual shale oil, showed a similar decrease in NO_x emissions, from 925 ppm unstaged to 175 ppm at a primary zone stoichiometric ratio of 0.7. The

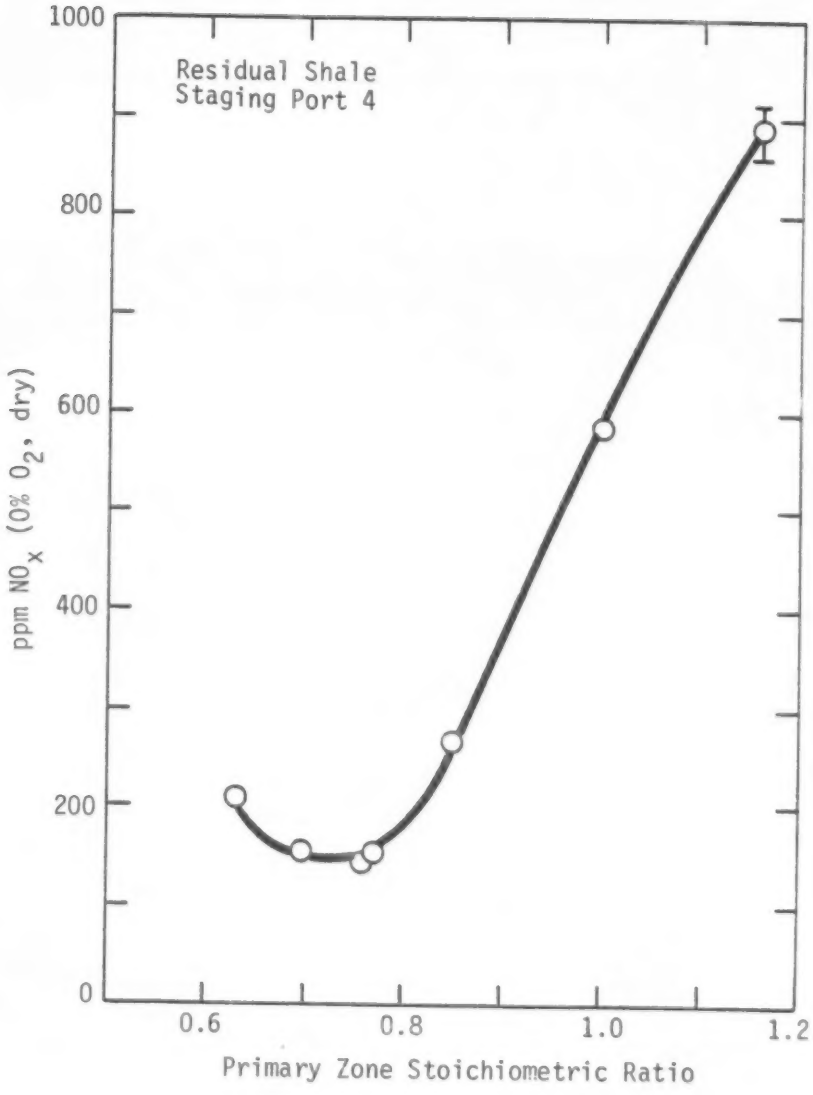


Figure 3-17. Staged results - residual shale oil (A5).

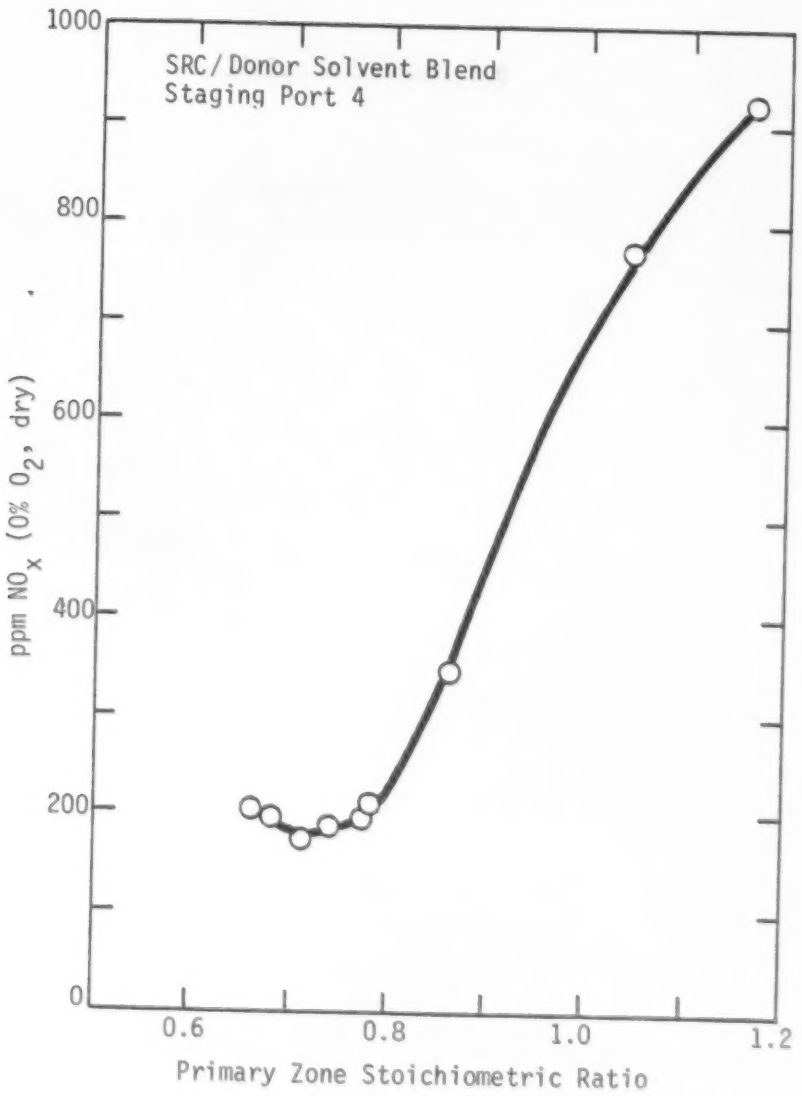


Figure 3-18. Staged results - SRC/donor solvent blend (A4).

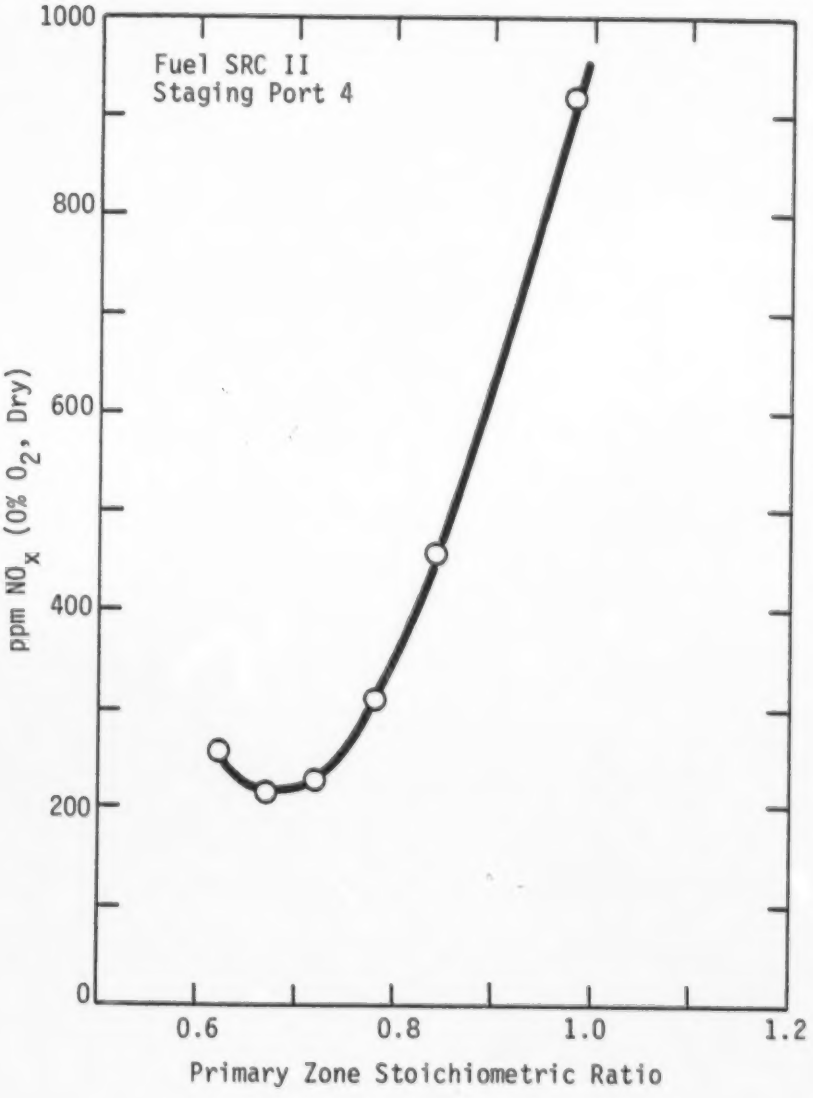


Figure 3-19. Staged results - SRC II (A6).

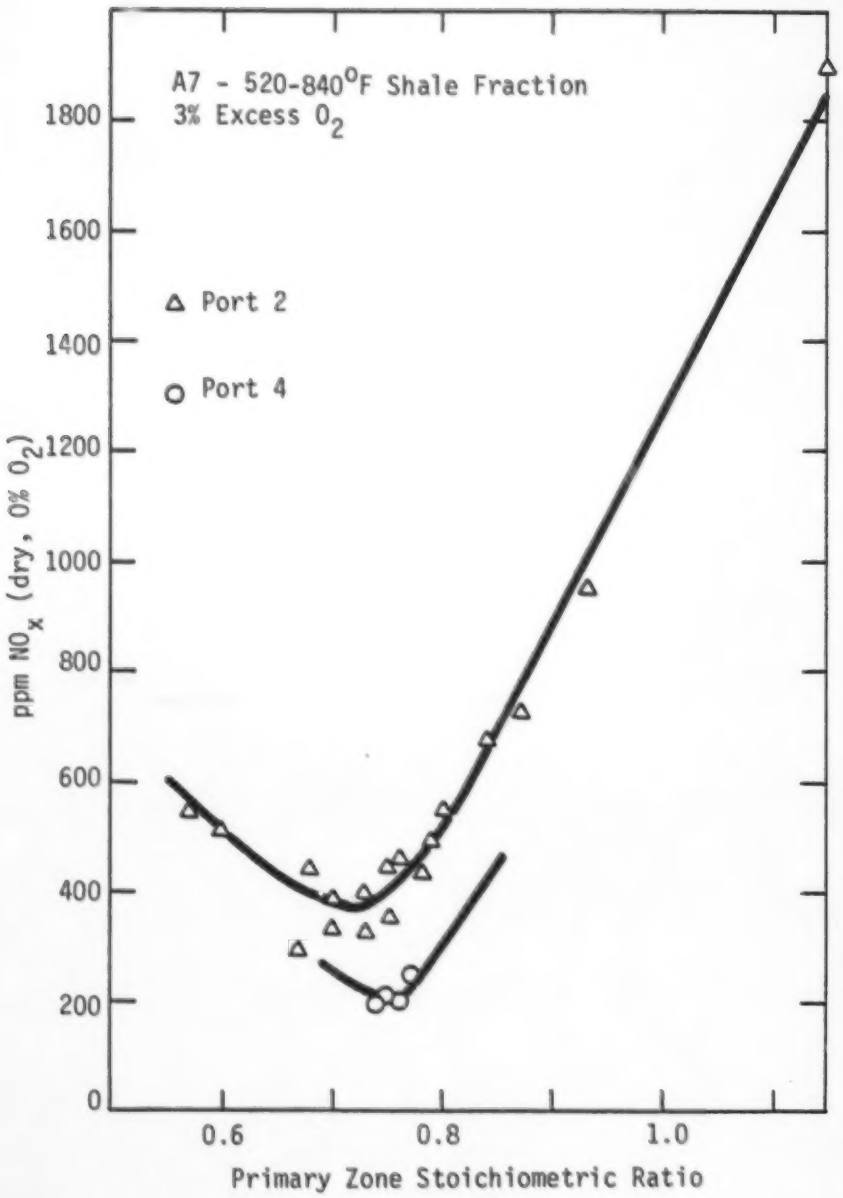


Figure 3-20. Staged results - 520-840°F shale fraction (A7).

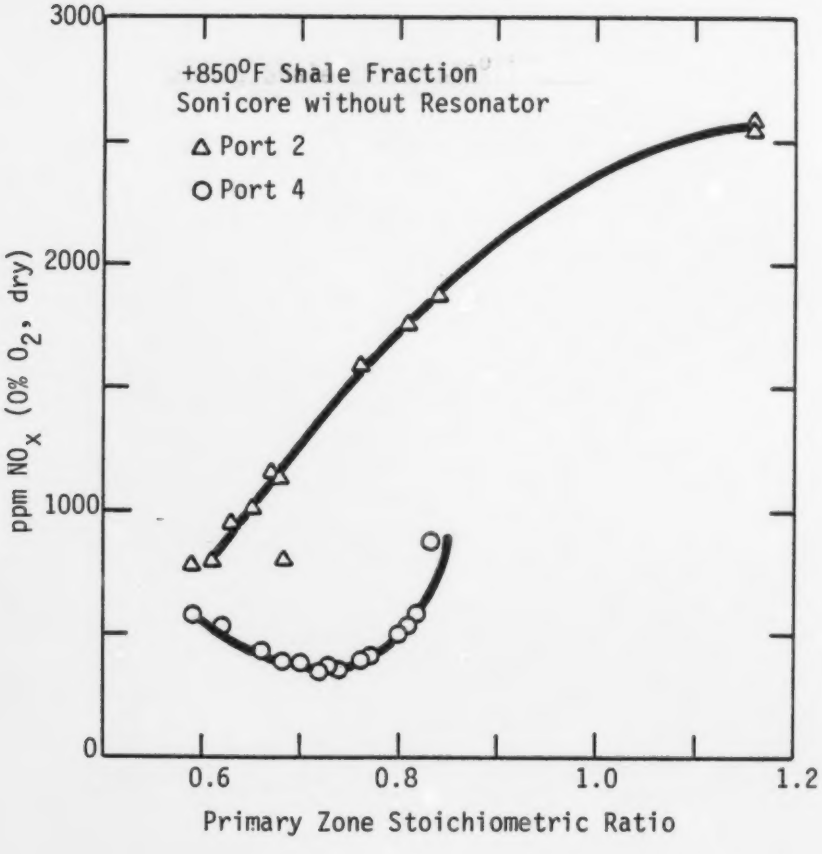


Figure 3-21. Staged results - +850°F shale fraction (A8).

minimum NO level for the SRC/donor solvent blend was slightly higher than was obtained with the residual shale oil. This may be due to the origin of the fuel and the nature of the fuel nitrogen compounds.

Figure 3-19 shows the effect of primary zone stoichiometry on NO_x emissions for the coal-derived SRC II fuel containing approximately 1 percent fuel nitrogen, staged at 400 msec primary zone residence time. A minimum NO level of approximately 21[illegible] ppm was obtained.

Figure 3-20 shows the effect of primary zone stoichiometric ratio on NO_x emissions for the 520-840°F shale fraction, for two primary zone residence times. Minimum emissions of approximately 360 ppm were obtained at a primary zone residence time of 400 msec (Port 2). Minimum NO_x emissions of 210 ppm were obtained at 800 msec residence time (Port 4).

Figure 3-21 shows the effect of primary zone stoichiometry and residence time on NO_x emissions from the heavy shale fraction. Since the alphaltene content and Conradson carbon residue were very high for this fuel, coke formation on the ultrasonic atomizer resonator tip occurred repeatedly after a very short period of time. In order to alleviate the coking problem, the resonator cap was removed from the nozzle. Also, because of the very high viscosity of the fuel, fuel temperature was raised to approximately 422 K in order to reduce viscosity sufficiently for good atomization. However, viscosity could not be reduced to 14 cst, since raising the fuel temperature beyond 422 K resulted in vaporization and cracking of the fuel within the oil gun. Previous work had shown that the impact of atomization parameters on NO_x emissions under staged combustion conditions was small with normal residual fuel oils. Minimum NO_x emissions below 750 ppm could not be achieved at 400 msec primary zone residence time. At 800 msec, the minimum NO_x level was approximately 350 ppm. Although this represents a reduction in NO_x emissions by 88 percent from unstaged conditions, the level is much higher than expected. This may be related to the refractory nature of the fuel nitrogen.

Figure 3-22 summarizes the minimum emission levels observed with the various fuels tested. In general minimum NO_x emissions increased with fuel nitrogen content up to approximately 200 ppm beyond which NO_x emissions were relatively insensitive to fuel nitrogen content. Two exceptions were observed. The methane/ammonia mixture, which represents the limit of volatility for a liquid fuel, produced much lower NO emissions than a liquid fuel of similar nitrogen content. The heavy shale fraction, on the other hand, produced much higher NO_x emissions than anticipated on the basis of fuel nitrogen content alone. These results imply that fuel nitrogen and fuel volatility may impact the minimum level of NO achievable under staged combustion conditions, since the actual residence time which the fixed nitrogen compounds spend in the gas phase is determined by the rate at which they evolve from the fuel droplet and decompose into reactive species such as HCN and NH_3. These results are consistent with the findings of the previous study[3.3]. Based on these results it can be concluded that the effect of staged combustion on NO_x emissions is similar for most petroleum-derived and synthetic liquid fuels, except for very heavy fuels where the evolution of fuel-bound nitrogen may be retarded.

3.4 Staged Combustion Optimization

This section deals with experiments to study the influence of stoichiometry, residence time, temperature, and mixing due staged combustion of liquid fuels. The objective of the experiments, conducted in the modified tunnel furnace shown in Figure 3-2, was to provide information which would allow the optimum environment history to be defined for minimizing NO_x emissions during the combustion of liquid fuels.

Staged heat release (staged combustion) provides the most effective NO_x control technique for nitrogen-containing fuels because fuel NO formation is mainly dependent upon local stoichiometry. It can be accomplished either by separating the combustion chamber into two zones and dividing the total combustion air into two streams, or by an appropriate burner design which promotes localized fuel-rich conditions. Under fuel-rich conditions, the efficiency of fuel nitrogen conversion to N_2 increases signifi-

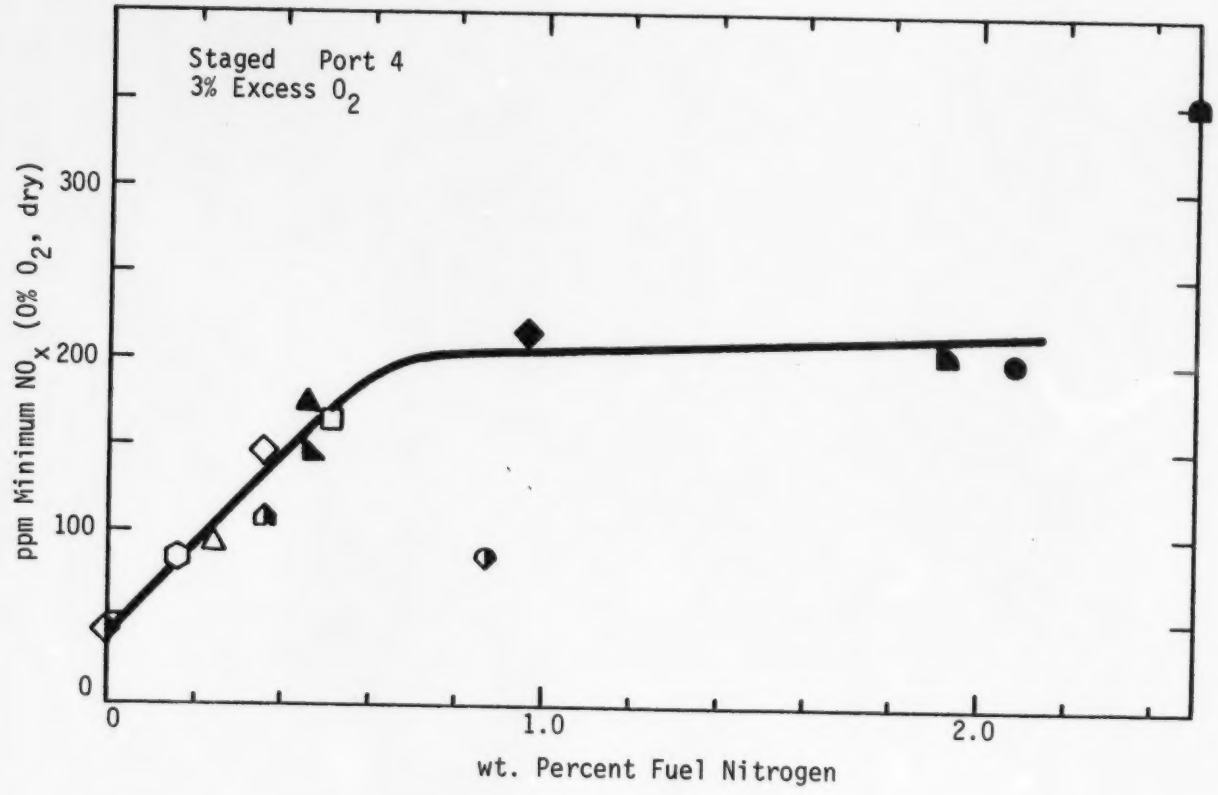


Figure 3-22. Comparison of minimum NO_x emissions achieved under staged combustion conditions for synthetic and conventional liquid fuels (400 msec primary zone residence time).

cantly(3.2-3.9). Thus, there are two overall fuel nitrogen reaction paths leading to the production of N_2 or NO, namely:

Path A. Fuel Lean

$$XN + \text{Oxidant} \longrightarrow NO + \ldots$$

Path B. Fuel Rich

$$XN + \ldots \longrightarrow N_2 \ldots$$

The objective of staged combustion emission control techniques is the provision of conditions which maximize N_2 production via Path B. Two factors of practical importance are the residence time and the stoichiometry required to maximize N_2 production in the fuel-rich primary zone.

If the residence time is insufficient, then the original fuel nitrogen species will exist in the gaseous state as some XN compound which can be converted to NO in the second-stage heat release zone. The stoichiometry required to achieve minimum XN concentrations at the exit of the primary stage will be determined by (1) the rate of evolution of nitrogen species from the fuel; (2) the inevitable distribution of stoichiometries from fuel-rich to fuel-lean which occurs because the primary zone is supplied by a diffusion flame; and (3) the overall temperature of the primary zone. Figure 3-23 shows the results of equilibrium calculations for methane combustion with 1 wt percent nitrogen in the fuel[3.14]. As the flame zone stoichiometry is reduced below 1.0, the equilibrium NO decreases markedly and NH_3 and HCN begin to rise (Figure 3-23a). The minimum total fixed nitrogen (TFN = NO + HCN + NH_3) is a strong function of temperature as shown in Figure 3-23b. Increasing the temperature reduces the first stage stoichiometry at which the minimum occurs. In addition, below SR_2 = 0.9, equilibrium TFN concentrations are less than 10 ppm for all conditions for practical interest. Thus, in theory, it should be possible to produce very low levels of NO_x via staged combustion by driving the primary zone reactants toward equilibrium and by minimizing formation of thermal NO_x in the second stage. Thermal NO_x could be controlled, for example, by providing heat extraction to cool the primary zone products prior to the addition of second-stage air. In

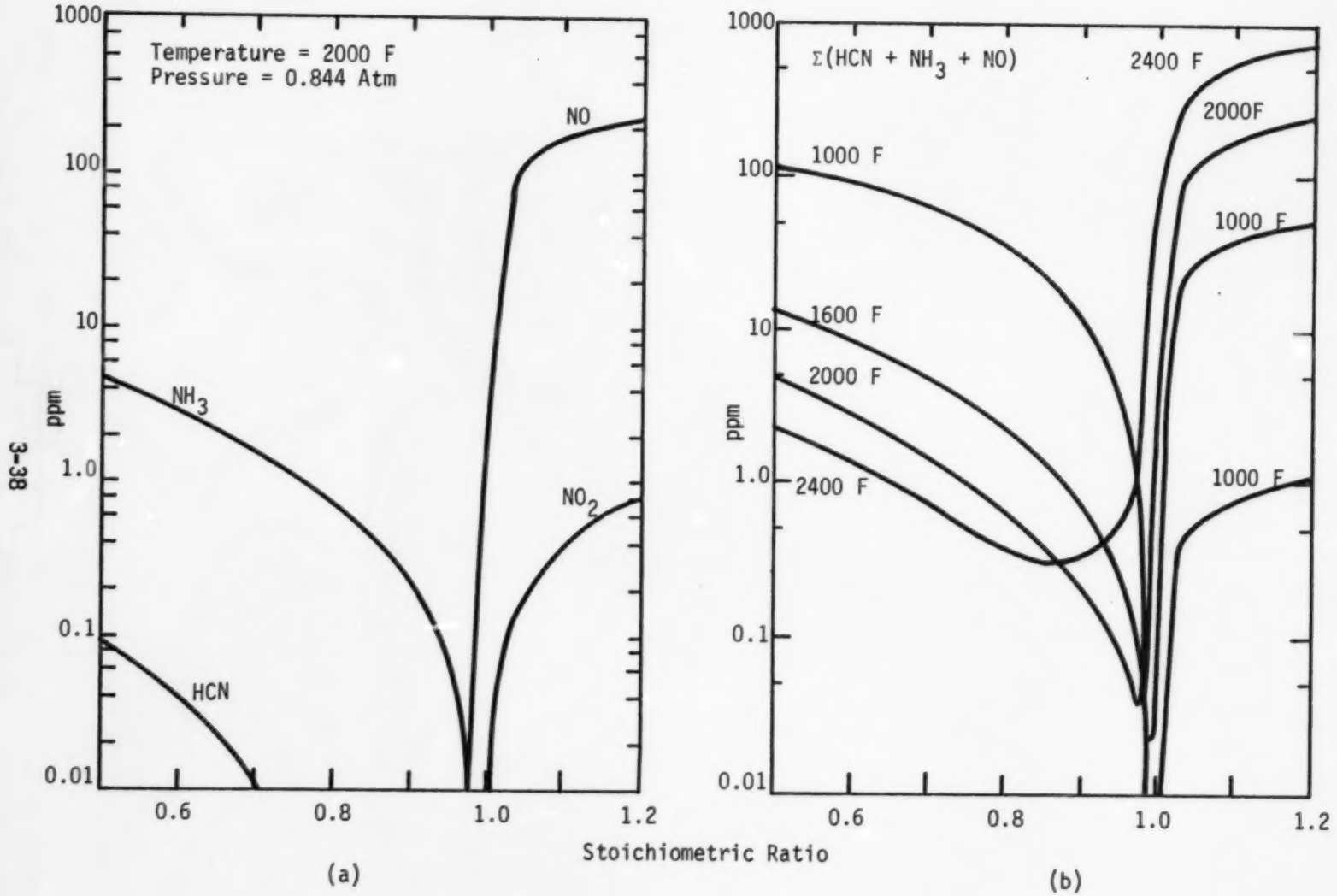


Figure 3-23. Equilibrium TFN concentrations.

a practical system interstage heat extraction must be optimized to cool the second stage flame sufficiently to minimize thermal NO but still maintain temperature sufficient to avoid quenching and emission of unburned carbon (soot), hydrocarbons, and carbon monoxide.

The scope of these experiments included:

- Exhaust gas species concentrations (O_2, CO_2, CO, NO);
- Detailed in-flame measurements of NO, HCN, NH_3, CO, O_2, hydrocarbons, and gas temperature;
- Variation of primary zone residence time, heat extraction (total and profile), and stoichiometry,;
- Two modes of secondary air injection;
- Eight liquid fuels, including Alaskan diesel oil (D1), Indo/Malaysian No. 6 oil (R4), Alaskan Bunker C oil (R9), Kern River Crude oil (R14), SRC II heavy distillate (A9), crude Paraho shale oil (A3), +850°F refined shale fraction, and Alaskan diesel oil doped with pyridine;
- One methane/ammonia gaseous fuel.

3.4.1 First Stage Stoichiometry

During fuel-rich combustion the original fuel nitrogen species are ultimately converted to N_2, HCN, NO or NH_3[3.6,3.7,3.8]. The intent of staged combustion is to minimize concentration of total fixed nitrogen (NH_3 + NO + HCN = TFN) prior to second-stage air addition. Figure 3-24 presents data obtained from detailed in-flame measurements for a distillate oil (D1 - Alaskan diesel), a typical residual oil (R9 - Alaskan Bunker C), and an alternate liquid fuel (A9 - SRC II heavy distillate). These measurements were made on the centerline of the furnace at a distance of 103 cm

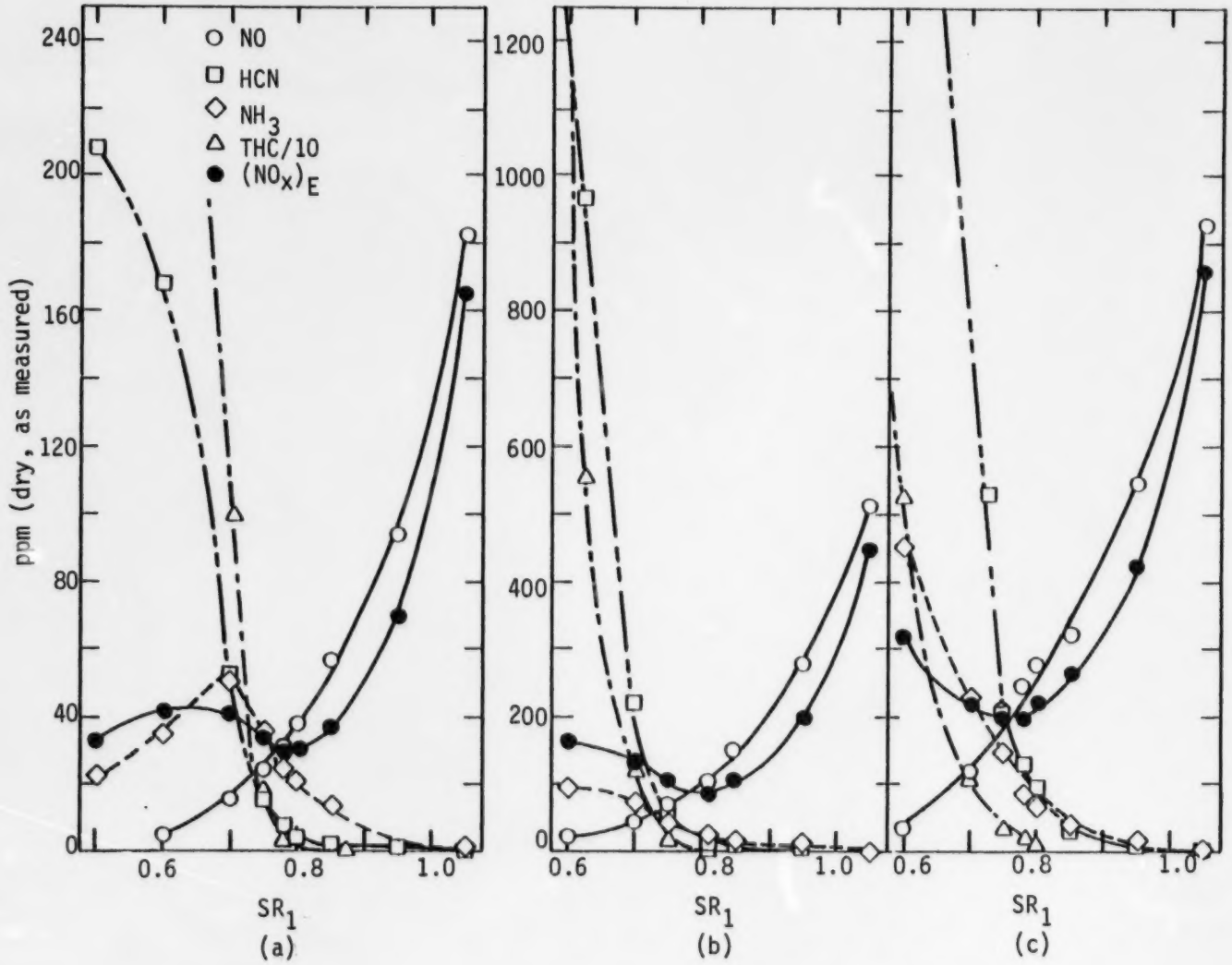


Figure 3-24. NO, HCN, NH_3, and HC production in the fuel rich hold-up zone for (a) D1 - Alaskan distillate oil, (b) R9 - Alaskan Bunker C oil and (c) A9 - SRC II heavy distillate oil (3 percent overall excess oxygen, 630 msec primary zone residence time).

(approximately 630 msec) from the oil nozzle. Detailed radial measurements indicated that the concentration profile was essentially uniform at this location. These in-flame data are reported on a dry, as-measured basis. Second-stage air was added at 107 cm subsequent to each in-flame measurement in these experiments to bring overall theoretical air to 116 percent, and exhaust NO_x measurements $(NO_x)_E$ are also shown (on a dry, 0 percent O_2 basis).

Decreasing the first-stage stoichiometry ratio reduced NO concentration leaving the first stage. However, below a stoichiometric ratio of approximately 0.8 significant amounts of hydrocarbons (THC) and HCN were measured. Thus, there exists a minimum in exhaust NO_x concentrations because of a competition between decreased first-stage NO and increased oxidizable nitrogen species such as HCN. It should be noted that HCN concentration increased rapidly below $SR_1 = 0.75$ and that this increase is accompanied by an increase in hydrocarbon content of the partially oxidized combustion products.

Data for the Alaskan diesel oil (Figure 3-24a) also show the presence of much smaller but significant concentrations of HCN and NH_3, although this fuel is essentially nitrogen-free. Total conversion of the fuel nitrogen would produce 15 ppm TFN at $SR_2 = 0.7$. This confirms previous work[3.7-3.8-3.9] which demonstrated that reactions involving hydrocarbon fragments and N_2 or NO can produce HCN. Figure 3-25 presents in-flame measurements with the Alaskan Bunker C and crude shale oils and with secondary air injection at 56 cm. This corresponds to a primary zone residence time of approximately 210 msec. The distribution of fixed nitrogen species and general trends with stoichiometry were similar to those at longer residence times; however, the absolute levels of NO, HCN, and NH_3 were much higher. This resulted in corresponding higher exhaust NO_x emissions.

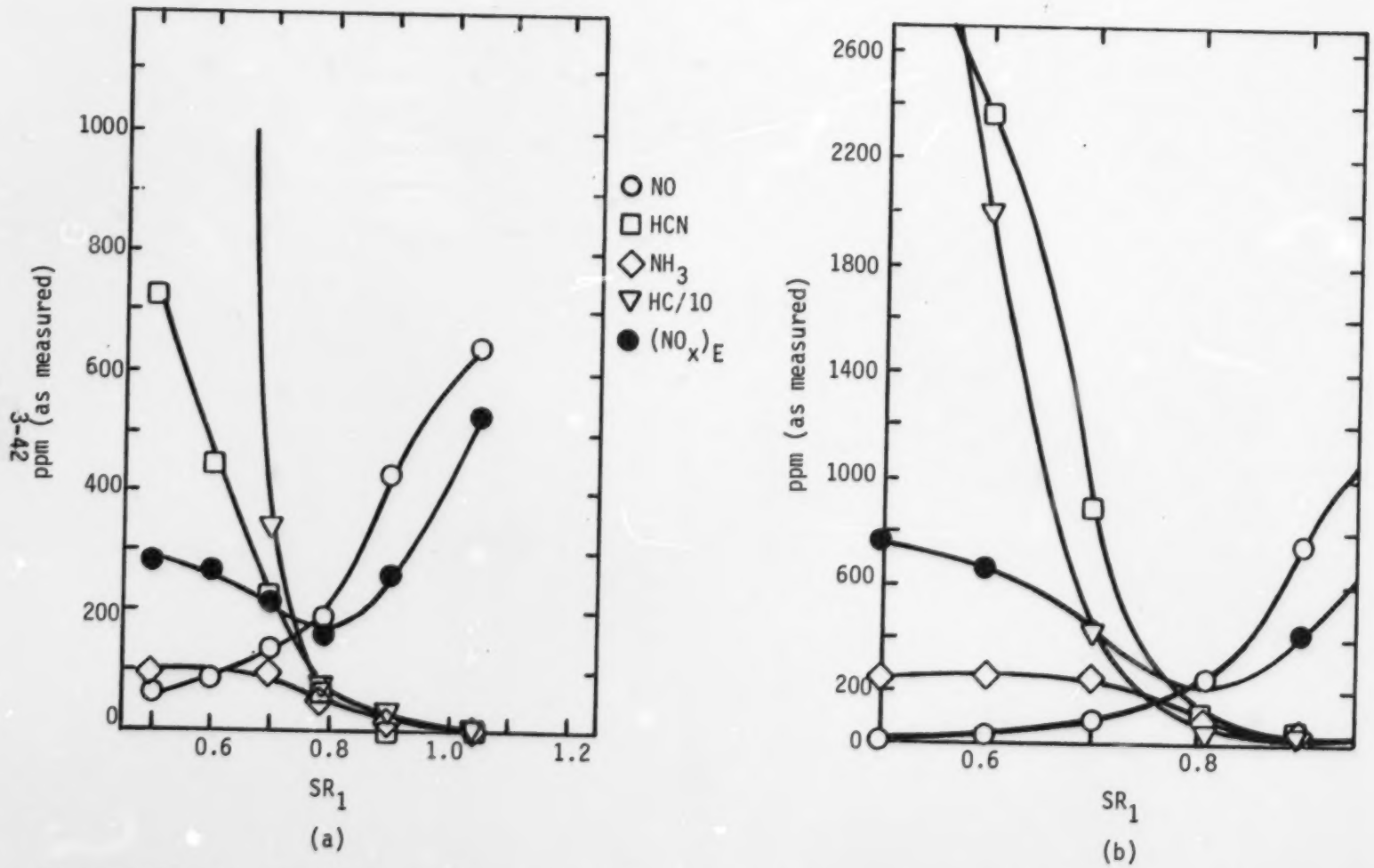


Figure 3-25. NO, HCN, NH_3, and HC production in the fuel rich hold-up zone for (a) R9 - Alaskan Bunker C and (b) A3 - crude shale (3 percent excess oxygen, 210 msec primary zone residence time).

3.4.2 Fuel Chemistry

Total Fixed Nitrogen

Total fixed nitrogen measured at the exit of the fuel-rich hold-up zone is presented in Figure 3-26 as a function of stoichiometric ratio for the Alaskan diesel oil, three petroleum-derived liquid fuels, three alternate liquid fuels, and methane doped with 0.79 weight percent nitrogen as ammonia. All fuels investigated showed similar trends. TFN reached a minimum concentration at approximately $SR_1 = 0.8$, and then increased significantly as the primary zone became more fuel-rich. The TFN for both the ammonia-doped methane and the fuel oil of similar nitrogen content (R14) showed similar characteristics under fuel-lean conditions. However, below $SR_1 = 0.7$ the heavy oil produces significantly less TFN than the gaseous fuel.

TFN Partition

Figure 3-27 shows the percentage of the original fuel nitrogen existing as either NO, NH_3 or HCN at various stoichiometric ratios for four fuels. Above $SR_1 = 0.8$, NO was the dominant TFN species; at lower stoichiometries HCN dominated except with the CH_4/NH_3. Axial profiles with the liquid fuels indicate that near $SR_1 = 0.8$, significant amounts of NH_3 may be formed early in the rich zone, but they decay rapidly. These data are in strong contrast to similar results obtained with pulverized coal[3.10] which indicate that the preferred TFN species is a strong function of coal composition.

In general, both the alternate and petroleum-derived liquid fuels behaved very similarly with the exception of the Kern County, California crude (R14). It produced less HCN under rich conditions, and this tendency cannot be readily associated with common fuel properties. Hydrocarbon and nitrogen distillation data indicated that in terms of equilibrium volatile evolution the Kern County fuel is intermediate among the liquids tested. The Indonesian oil was the lightest of the liquid fuels and it produced the highest TFN concentration at $SR_1 = 0.8$.

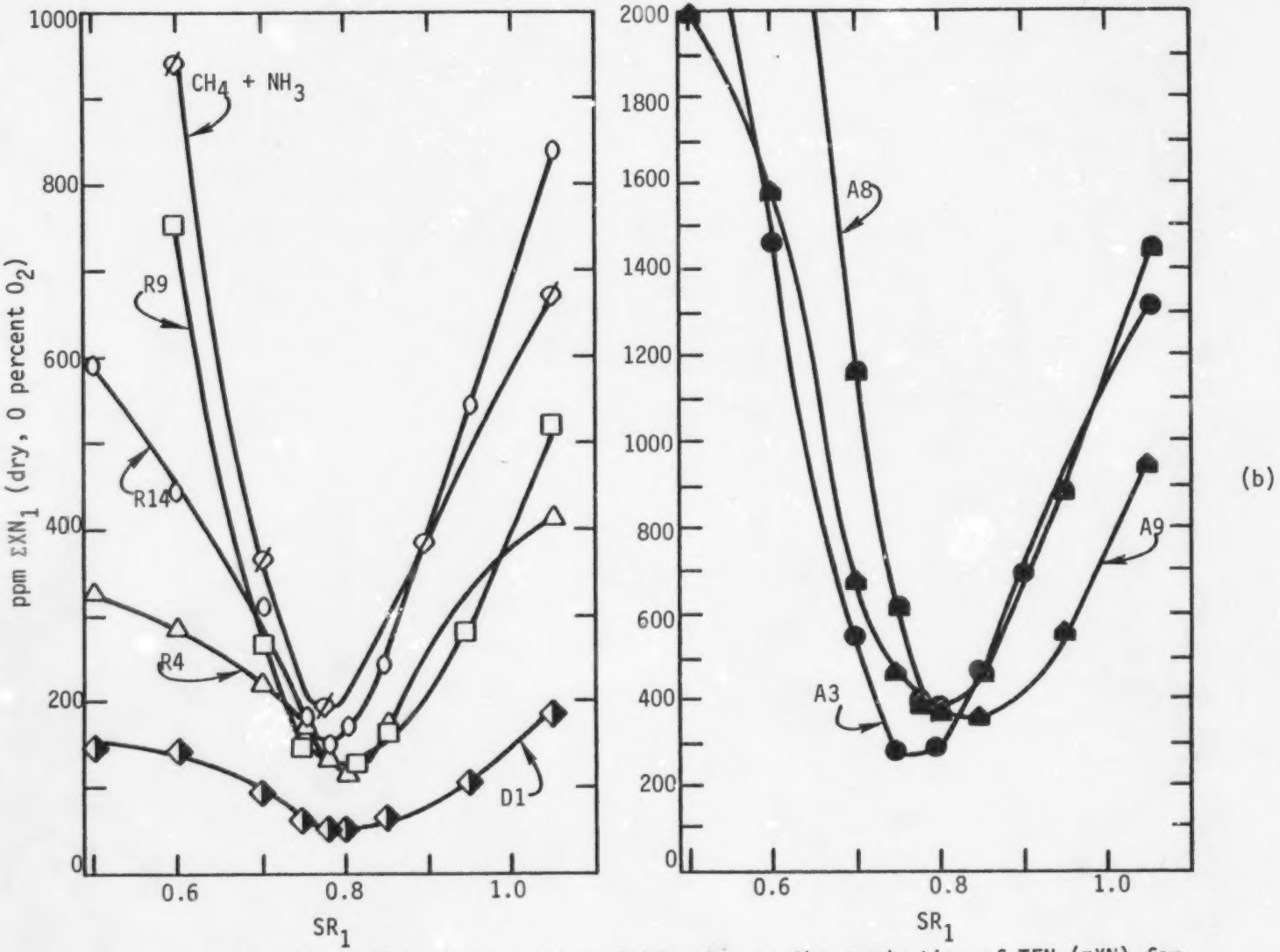


Figure 3-26. The effect of fuel type and stoichiometry on the production of TFN (ΣXN) for (a) petroleum oils and (b) alternate fuels.

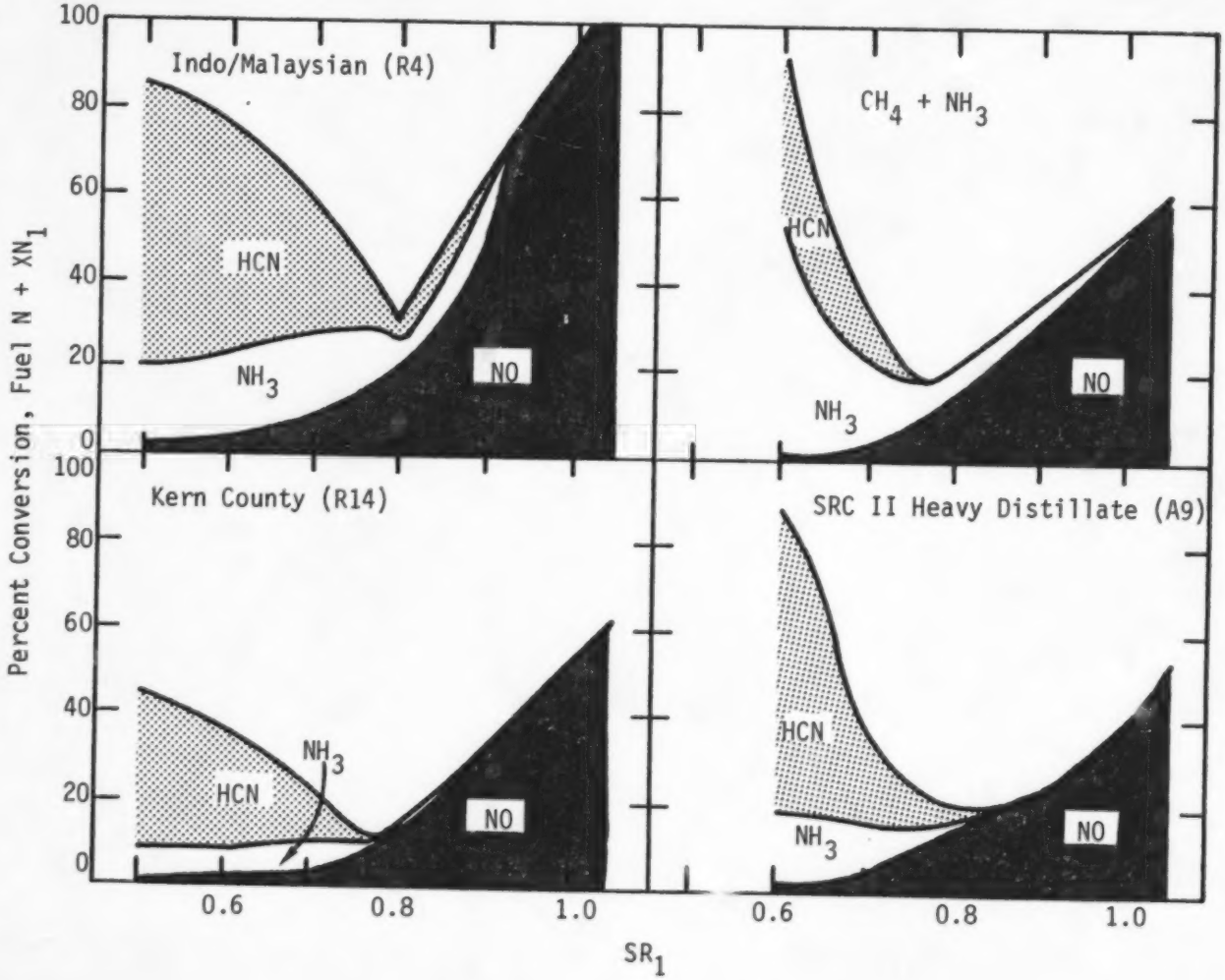


Figure 3-27. Distribution of first-stage XN species for alternative and petroleum derived fuels.

Figure 3-28 summarizes all of the TFN partition data as a function of the first-stage stoichiometric ratio. Data for the six liquid fuels and the 0.79 weight percent nitrogen (as NH_3) in methane gas are presented as the percentage of the original fuel nitrogen existing as HCN, NH_3 or NO at the end of the fuel-rich first stage. In each case the missing fuel nitrogen has either been converted to N_2 or still exists in some partially oxidized fuel fragment. All of the liquid fuels exhibited the same general trends:

- Above approximately SR_1 = 0.8, NO was the dominant TFN species.
- Below SR_1 = 0.75 the major TFN species was HCN and under very fuel-rich conditions HCN usually accounted for more than 50 percent of the initial fuel nitrogen.
- First-stage NH_3 levels are always low, generally less than 20 percent of the fuel N. Axial profiles indicated that near SR_1 = 0.8, significant amounts of NH_3 were formed early in the rich zone, but decayed rapidly.

The fraction of fuel nitrogen converted to HCN was somewhat less for the CH_4/NH_3 mixture (⌀) than for most of the liquid fuels tested (Figure 3-28a); however, as expected, conversion to NH_3 (Figure 3-28b) and NO (Figure 3-28c) was higher than the liquid fuels. The light (API = 21.8) Indonesian/Malaysian residual oil (△) produced consistently higher conversion of fuel nitrogen to HCN, NH_3 and NO than the much heavier (API = 12.3) Kern County crude oil (○). Conversely, conversion to HCN and NH_3 for the +850°F shale residuum (■) was higher than for the lighter parent crude shale (●); however, conversion to NO was lower. The exact relationship of simple fuel properties to conversion of fuel nitrogen to intermediate XN species is not apparent at this time.

Hydrocarbons

The rapid increase in HCN concentration below SR_1 = 0.8 was accompanied by an increase in hydrocarbon content of the partially oxidized combustion

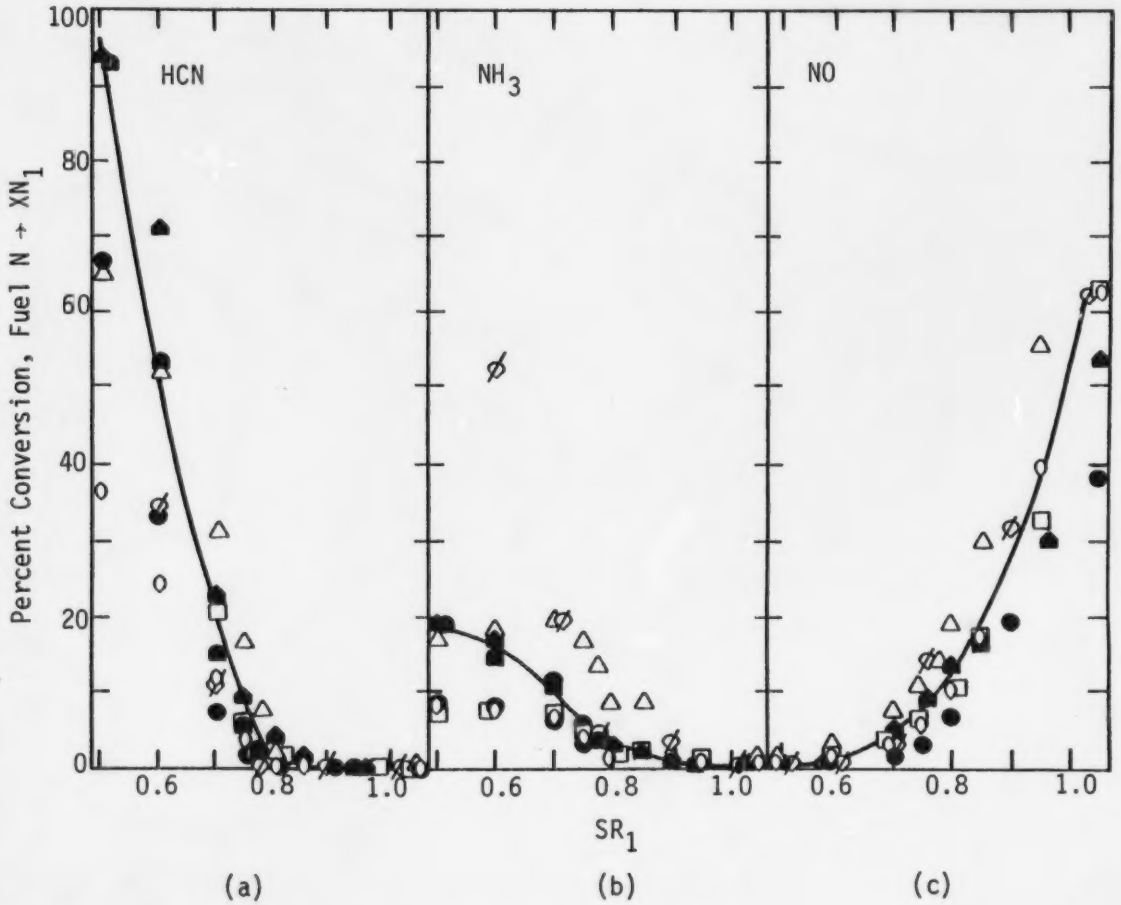


Figure 3-28. The conversion of fuel bound nitrogen to XN.

products. Figure 3-29 summarizes the in-flame hydrocarbon measurements for the Alaskan diesel (D1), three petroleum-derived residual oils (Indonesian - R4, Alaskan - R9, Kern County - R14), three alternative liquids (SRC II heavy distillate - A9, crude shale - A3, heavy shale fraction - A8) and methane containing 0.75 weight percent nitrogen as NH_3 (⊘). Hydrocarbon concentrations correlate well on the basis of first-stage stoichiometry. At very low stoichiometric ratios the distillate oil (◆) and CH_4/NH_3 produced slightly higher hydrocarbon concentrations than the heavier liquid fuels.

3.4.3 Second-Stage Processes

Exhaust NO_x emissions in a staged combustor result from conversion of TFN exiting the first stage and any thermal NO production during burnout. Second-stage thermal NO_x production is not considered to be significant in this study because changes in heat extraction during burnout had almost no effect on final emissions. Figure 3-30 shows minimum exhaust NO_x and the associated TFN as a function of total fuel nitrogen content for the seven liquid fuels and the CH_4/NH_3. In general, the minimum exhaust NO_x and the associated TFN as a function of total fuel nitrogen content for the seven liquid fuels and the CH_4/NH_3. In general, the minimum exhaust NO_x concentration occurred at $SR_1 = 0.78 \pm 0.02$. Under these optimum staged conditions NO_x emissions (and TFN) correlate well with total fuel nitrogen content, but the slope is significantly less than under excess air conditions. Only the SRC II heavy distillate (▲) exhibited unusually high emissions, and this was the direct result of a high TFN yield (Figure 3-30b). NO, NH_3 and HCN were all substantially higher for this fuel than with comparable fuels at the minimum stoichiometry (0.78). The increased TFN may be the result of basic chemical bonding differences between the parent coal from which the SRC II was derived and petroleum liquids.

Figure 3-31 shows the percent of the TFN exiting the first stage which was converted to NO_x in the second stage (based on NO_x measured in the furnace exhaust). Data for all eight fuels and first-stage stoichiometries between 0.5 and 0.8 have been included. As the TFN concentration increased (due to decreasing SR_1), the percentage conversion decreased. This behavior

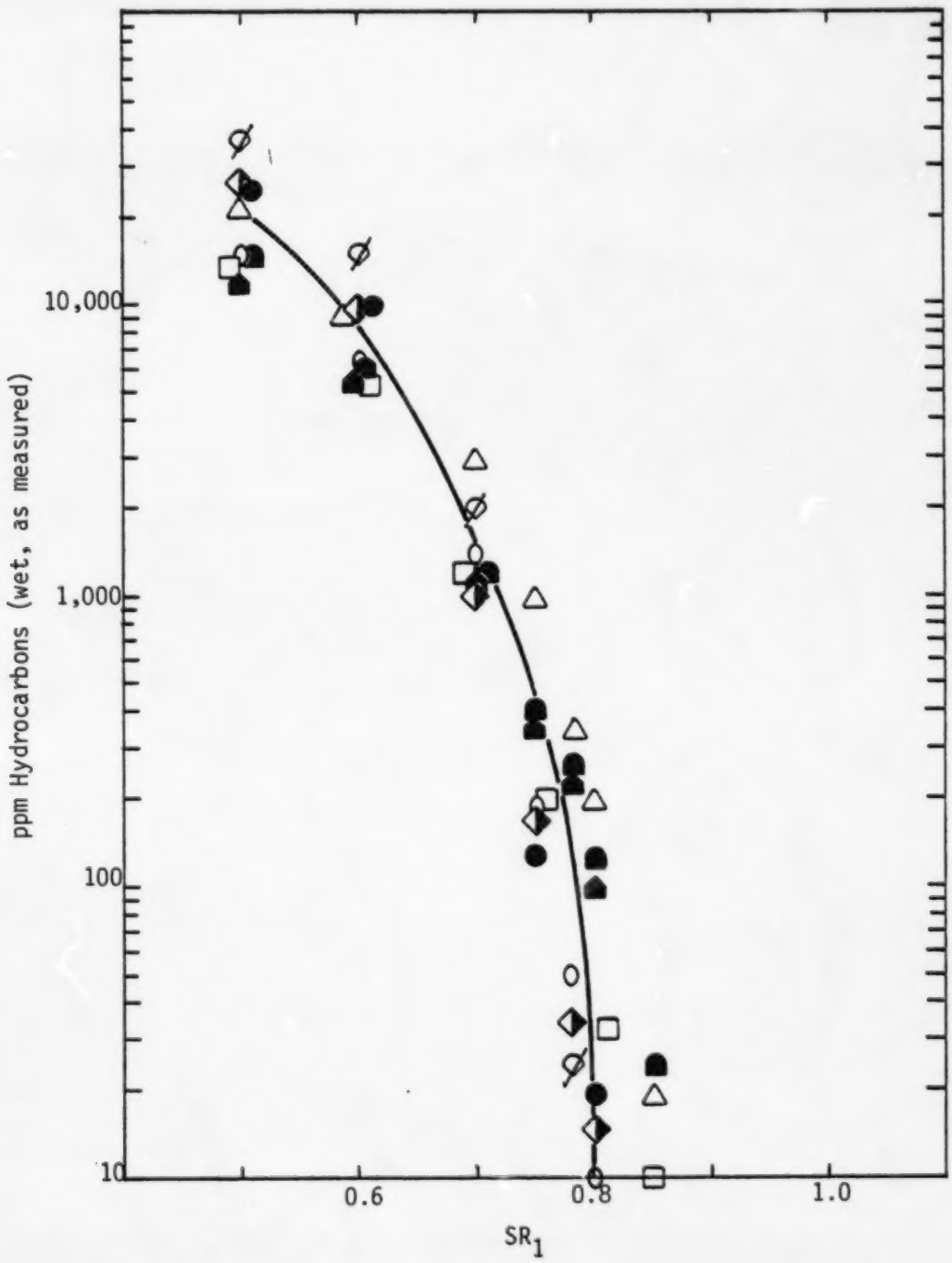


Figure 3-29. First stage hydrocarbon production.

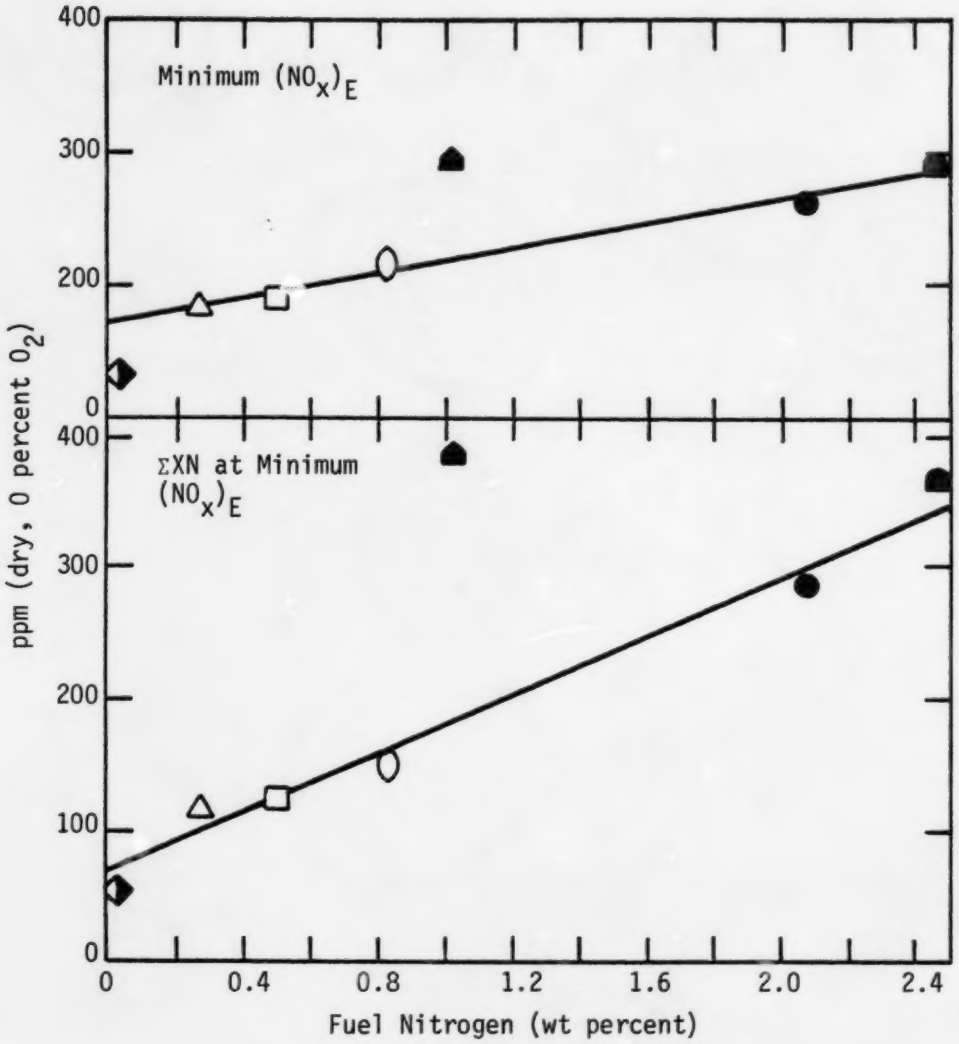


Figure 3-30. The effect of fuel bound nitrogen content on exhaust NO_x and TFN (ΣXN) in the primary zone at SR_1 = 0.7 (3 percent overall excess O_2).

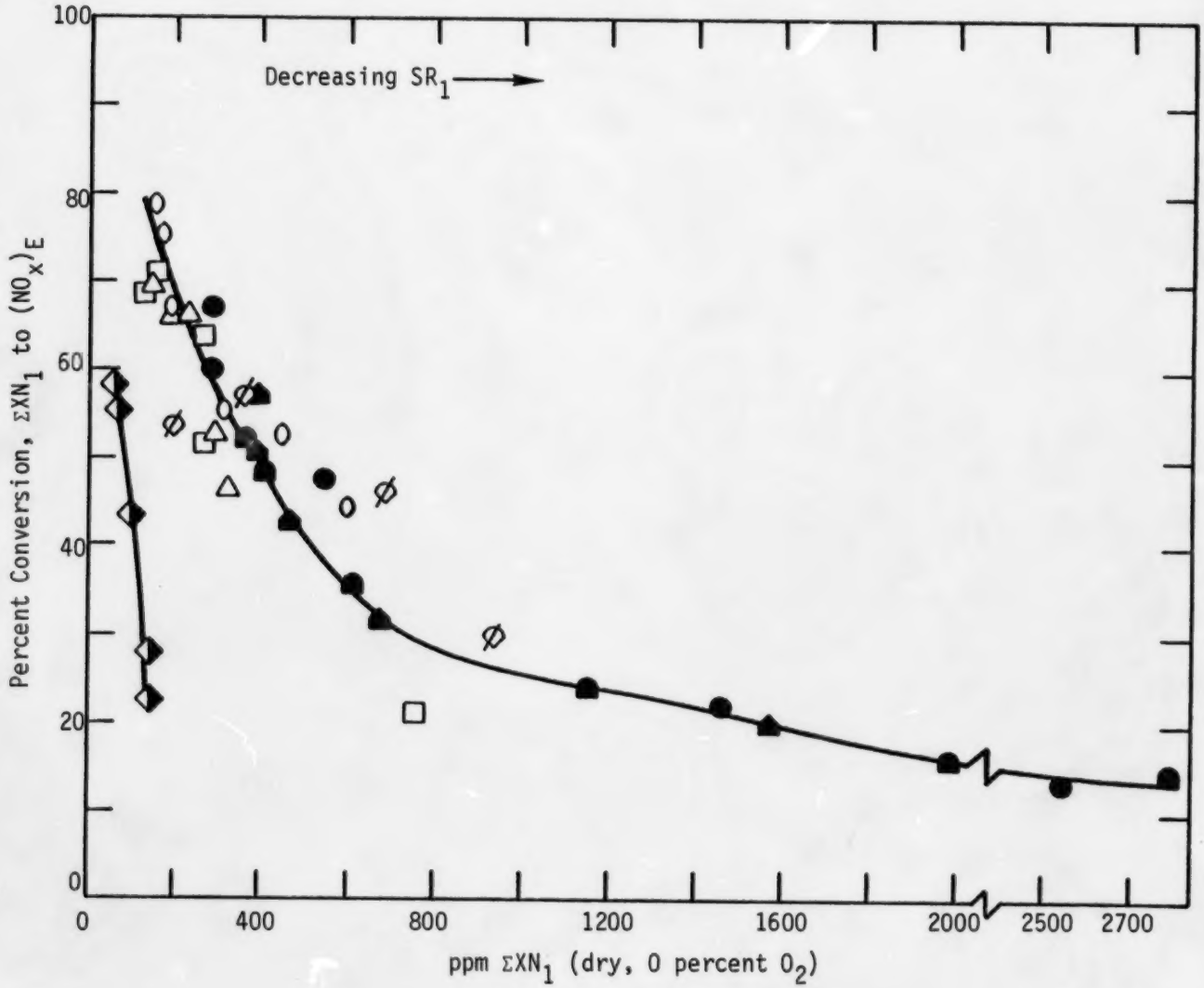


Figure 3-31. Conversion of TFN to exhaust NO_x.

is analogous to that reported previously for poorly mixed excess air diffusion flames[3.15-3.16]. The second-stage burnout can be considered an excess air flame with a gaseous, hydrocarbon fuel. The general conversion decrease may be the result of a competition between N_2 formation reactions which are second order in XN and first order NO formation reactions.

The distillate oil results (◆) in Figure 3-31 are substantially below all of residual petroleum and alternative liquid data and the CH_4/NH_3 results are slightly high. This suggests that TFN conversion is also dependent on the nitrogen speciation and/or the oxidation of the partial products of combustion at the exit of the fuel-rich zone. At the TFN = 145 ppm point, the first-stage exhaust from the distillate oil contained 10,000 ppm hydrocarbons and the dominant TFN species was HCN (SR_1 = 0.6). In contrast, the comparable heavy oil points had less than 400 ppm hydrocarbons and NO was the major TFN species (SR_1 = 0.78).

3.4.4. Time/Temperature History

The TFN concentrations shown in Figure 3-30 are in excess of equilibrium levels, and Sarofim and co-workers[3.11] have suggested that increasing the temperature of the primary zone would prove beneficial. The results presented in Figures 3-32 and 3-33 obtained with the shale crude (A3) demonstrate the impact of first-stage heat loss on the fate of fuel nitrogen. The hot conditions refer to the furnace without primary zone cooling and with the radiation choke (as shown in Figure 3-24). To cool the furnace, cooling coils were added prior to the second-stage choke and the radiation choke was removed. Figure 3-32 shows exhaust NO_x and primary zone gas temperature as a function of stoichiometric ratio for the two conditions. Minimum NO_x emissions were reduced for the hot case, and the optimum stoichiometry was shifted toward more fuel-rich conditions.

The axial profiles presented in Figure 3-33 provide an explanation for this shift in the minimum emission levels. Heat extraction in the first stage impacts the rate of decay of TFN. Under cold conditions both NO and HCN essentially freeze, whereas without heat extraction the initial rate of

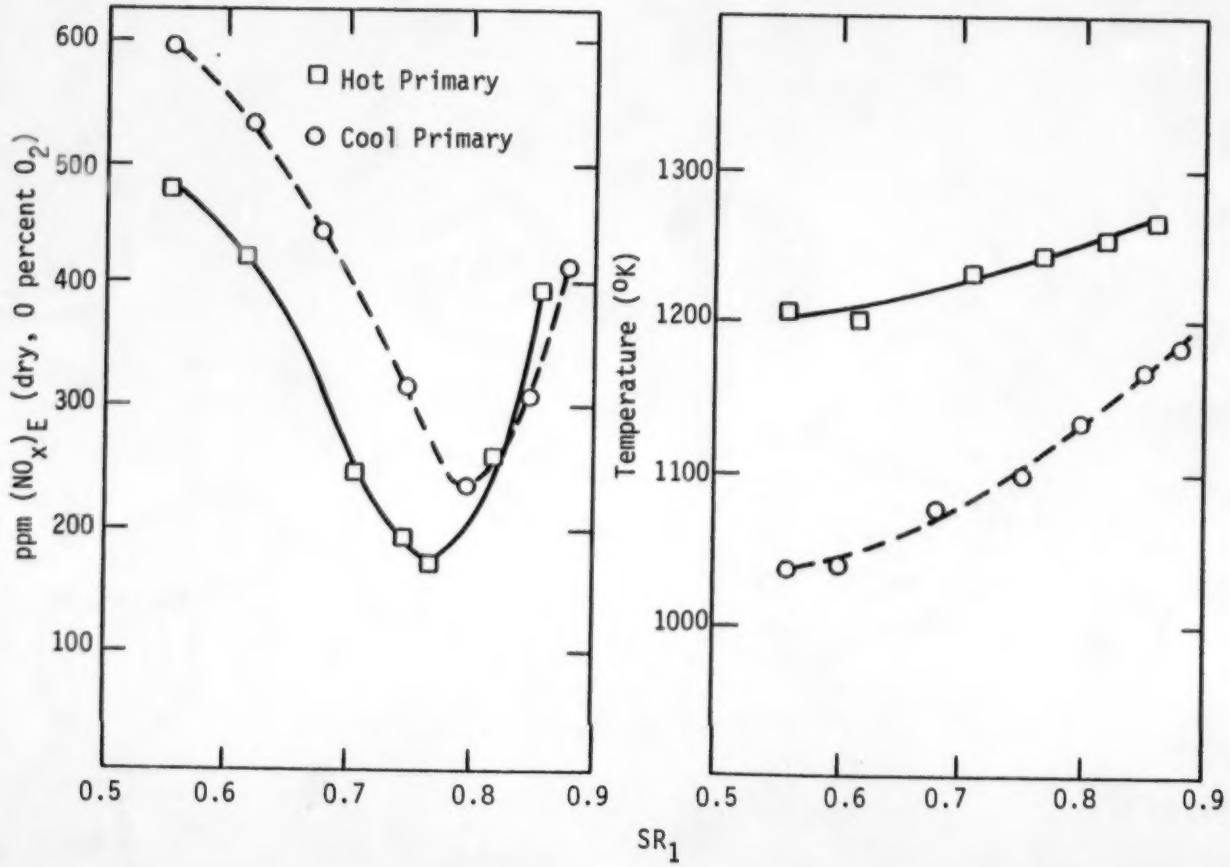


Figure 3-32. The influence of fuel rich hold-up zone temperature profile on exhaust NO_x.

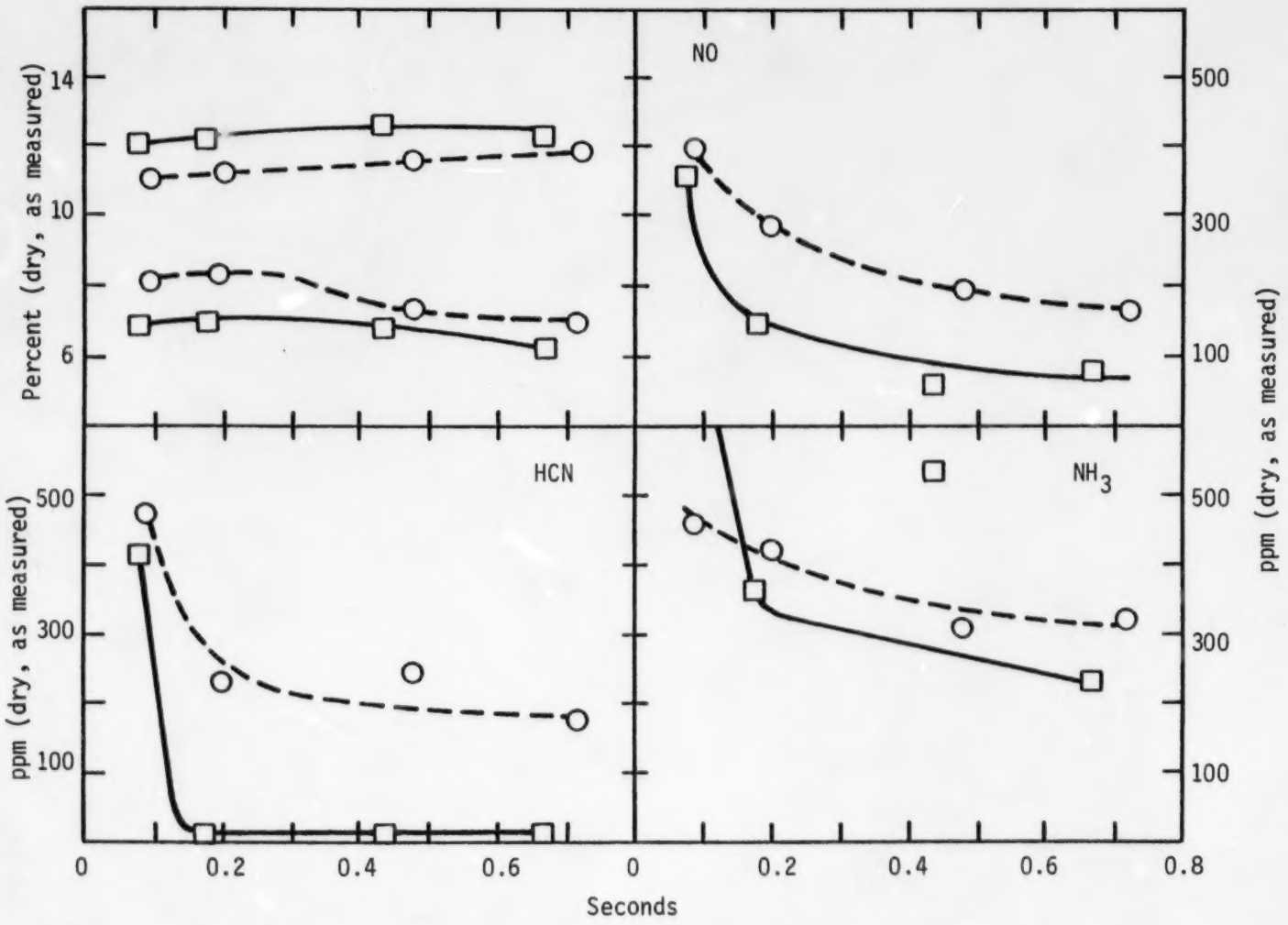


Figure 3-33. CO oxidation and decay of XN species for two temperature profiles.

decay for all three species is much faster, leading to low TFN concentrations at the exit of the fuel-rich first stage. It should be noted that heat extraction also affects the rate of CO oxidation.

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